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AD NUMBER
AD379516

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TO: unclassified
FROM: confidential

LIMITATION CHANGES
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AUTHORITY
31 Jan 1979, DoDD 5200.10; AFRPL ltr, 18 Jan 1980

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AFRPL-TR-67-18

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INVESTIGATION OF THE MECHANISM

OF SOLID PROPELLANT BURN RATE

Contract AF04(611)-11212

FINAL TECHNICAL REPORT AFRPL-TR-67-18
January 1967

David A. Flanigan
Huntsville Division
Thiokol Chemical Corporation

Air Force Rocket Propulsion Laboratory
Research and Technical Division
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United States Air Force
Edwards Air Force Base, California 93523

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INVESTIGATION OF THE MECHANISM
OF SOLID PROPELLANT BURN RATE

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FINAL TECHNICAL REPORT AFRPL-TR-67-18

David A. Flanigan

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UNCLASSIFIED FOREWORD

This, the Final Technical Report under Contract No. AF04(611)-11212, covers the work performed from 15 November 1965 through 14 November 1966. This contract with the Huntsville Division of Thiokol Chemical Corporation was initiated under Air Force Rocket Propulsion Laboratory, Research and Technology Division Project No. 3148. It was accomplished under the technical direction of R. W. Bargmeyer, 1/Lt, USAF of the Research and Technology Division, Air Force Systems Command, United States Air Force, Edwards Air Force Base, California, 93523. Work in this technical area is being continued under contract F04611-67-C-0034.

Mr. G. F. Mangum of Thiokol - Huntsville Division's Project Management Directorate was Project Manager for this program. Dr. David A. Flanigan of the Research and Development Department was the Principal Investigator and Mr. Carl J. Whelchel of the Project Management Directorate was Assistant Project Manager. Others who cooperated in the work and in the preparation of this report are Messrs. Merle W. Larimer and Bonnard A. Allen, Research and Development Department, Mr. L. H. Caveny of the Engineering Department, and Mrs. E. J. Grice, Project Management Directorate. This report has been given the Thiokol internal report number 60-66 (Control No. C-66-60A).

This project was accomplished as a part of the Air Force program, the overall objective of which is to achieve the ability to tailor the burning rate of a propellant to any desired level in the range from 1 to 10 inches per second. This was to be accomplished with the addition of a minimum amount of an additive without adversely affecting the mechanical, ballistic, or safety properties of the propellant. The specific objective of this program was to determine the chemical mechanism by which materials such as iron oxide, ferric ferrocyanide, ferrocene, and ferrocenyl derivatives increase the burning rate of ammonium perchlorate oxidized propellants.

This report contains no classified information extracted from other classified documents.

STATEMENT OF APPROVAL

This technical report has been reviewed and is approved.

W. H. EBELKE, Colonel, USAF
Chief, Propellant Division

CONFIDENTIAL ABSTRACT

The mechanism by which iron compounds catalyze the burning rate of solid composite propellants is reported. A series of experiments were conducted to define the efficacy of iron compounds on burning rate. Experiments performed under Phases I and II studies, which were designed to study the interaction, if any, between catalysts and oxidizer and binder indicate the following conclusions. Thermal decomposition of ammonium perchlorate under pressure occurs in a single-phase step instead of the three phases observed at atmospheric pressure. The single-phase decomposition step of ammonium perchlorate is shifted to lower temperature in the presence of iron oxide. The degree of this shift is dependent upon Fe_2O_3 concentration. The autoignition temperature of composite propellant decreases with increasing pressure. The rate of decomposition of anhydrous perchloric acid on varied surfaces seems to be a strong function of exposed specific surface of the catalyst and not overly dependent upon the chemical nature of the material. Iron compounds such as Fe_2O_3, ferrocene and butyl ferrocene do not facilitate the pyrolysis of polybutadiene polymers or gumstocks. A mechanism for catalysis by iron compounds is presented and mathematical expressions relating the variables involved have been formulated.

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NOMENCLATURE

Lation Symbols	Definition	Unit
A	area	cm^2
B_s	linear pyrolysis rate law coefficient	$cm/sec\,^oK^{-\beta}$
c	specific heat	$cal/gm\,^oC$
E	activation energy	kcal/mole
f	function of cross-sectional area	
k	thermal conductivity	$cal/cm\,sec\,^oC$
$\dot{q}$	rate of heat transfer per unit of surface area	$cal/cm^2\,sec$
$\dot{q}'$	energy per unit volume from chemical reactions	$cal/cm^3\,sec$
$\dot{q}_{rad}$	energy per unit area from radiative sources	$cal/cm^2\,sec$
$\dot{q}_s$	heat evolution associated with chemical reactions and phase changes at the surface	$cal/cm^2\,sec$
Q_c	heat evolution accompanying a chemical or physical change	cal/gm
r	burning rate	cm/sec
R	gas constant	$1.9867\,cal/mole\,^oK$
T	temperature	^oK
T_f	flame temperature	^oK
t	time	sec
v_g	gas velocity at the surface, equal to the normal burning rate (r) times the condensed phase density (ρ) divided by the density of the hot combustion gases (ρ_g) or: $$v_g = r_b \rho_c / \rho_g$$	cm/sec

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Latin Symbols	Definition	Unit
x	normal distance from the surface	cm
Z	frequency factor	

Greek Symbols

α	thermal diffusivity, equal to the thermal conductivity divided by the product of the density and specific heat or:	
	$$\alpha = k / (\rho \, c)$$	cm^2/sec
β_1	temperature dependence of pre-exponential factor in linear pyrolysis law	
ρ	density	gm/cm^3
τ	the ratio of the difference between the temperature at the propellant surface (T_s) and the initial temperature of the propellant (T_0) to the difference between the temperature of the regressing surface (T_{pg}) and the initial temperature of the propellant or	

$$\tau = \frac{T_s - T_0}{T_{pg} - T_0}$$

Subscripts

b	binder
c	condensed phase
fzt	flame zone thickness
if	interface
g	gas phase
ox	oxidizer
pg	phase change at subliming surface
s	exposed surface
0	initial conditions of solid phase

x

SECTION I

INTRODUCTION

(U)   The use of iron compounds to effect an increase in the burning rate of ammonium perchlorate based composite solid propellants has been exploited since 1951. Not only iron oxide, but also iron chelates, ferrocene and ferrocene derivatives have been fully evaluated and incorporated into propellant systems. However, in spite of several postulations regarding the mechanism whereby such compounds enhance burning rate, a minimum of research into this question has been accomplished and the resulting data are somewhat meaningless. Therefore, this program of applied research was initiated with the goal of defining the mechanism of burn rate catalysis by iron compounds. Ability to predict techniques for attaining further increases in burn rate, direction for synthesis of more efficient catalysts, a more comprehensive knowledge of composite propellant deflagration, and the ability to tailor burn rates between 1 and 10 inches per second were considered as primary objectives.

(U)   The approach has been one of selecting those mechanisms considered most plausible in view of the experimental data previously generated. Then, through a series of experiments designed to simulate practical combustion conditions, lend credence or withdraw support to those available mechanisms.

(U)   The program to determine the mechanism by which iron compounds catalyze the burning rate of composite propellants was divided into the following three phases:

(U)   Phase I - Decomposition of Catalysts

(U)   In order to ascertain what iron species exist at different points in the temperature profile of the flame zone and to determine what iron containing decomposition products are available for reaction as catalysts, a knowledge of the thermal decomposition of the catalysts themselves, as well as the oxidative degradation of each material will be required. Phase I experiments were designed to determine the products of decomposition of selected iron containing catalysts as well as ease of oxidation and effect of temperature and pressure variation on the products.

(U)   Phase II - Decomposition of Catalysts with Propellant Ingredients

(U)   Upon completion of Phase I studies, the role of iron containing catalysts in the decomposition of various conventional propellant ingredients were determined. Studies under this phase were conducted in three major areas as follows:

(U)   Task A - Iron Catalysts Effects of Ammonium Perchlorate
                     Decomposition

(U)   This area of investigation is an important facet of the research inas-
much as it is generally assumed that the efficacy of iron compounds is due to
their catalysis of, or interaction with, ammonium perchlorate decomposition.
The following studies will be conducted under this task.

(U)   Part 1 - Electron Transfer Studies

(U)   Experiments conducted under this study were designed to determine if
iron compounds catalyze an electron transfer reaction in the decomposition of
ammonium perchlorate. The question of whether solid phase catalysis occurs
is the important observation to be made in this phase.

(U)   Part 2 - Complex Formulation Studies

(U)   A series of experiments were performed to ascertain the validity of
the theory that ammonia is removed from the atmosphere of the decomposing
ammonium perchlorate, thus allowing favorable circumstances for decom-
position of perchloric acid.

(U)   Part 3 - Perchloric Acid Decomposition Catalysis

(U)   a.   Proton Transfer Studies

(U)   A series of experiments were performed to answer questions regarding
the proposed mechanism of perchloric acid decomposition catalysis. Basically,
this theory says that iron oxide does not enter any reaction but serves simply
as a reaction site for the more rapid decomposition of perchloric acid.

(U)   Task B - Iron Catalysts Effects on Binder Composition

(U)   The study of the decomposition of binders and the effects of this pyrolysis
on burning rate of composite propellants has been long neglected. The decom-
position products of the pyrolysis reaction are not known. The fact that ferrocene
and ferrocene derivatives have been shown to be excellent combustion catalysts
for hydrocarbons has placed even more emphasis in this mechanistic effect
of ferrocene on binder pyrolysis and to elucidate the basic pyrolysis mechanism
of polybutadiene polymers.

(U)   Task C - Iron Catalysts Effects on Aluminum Combustion

(U)   The possibility that either iron oxide or ferrocene will react with hot
molten aluminum in an oxidizing atmosphere has not been considered on com-
bustion studies of solid propellants. It is known that under certain conditions
a Thermit reaction can occur between iron oxide and aluminum. Such a

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reaction is very exothermic and would add substantial quantities of heat to the surface. Experiments were performed to determine if the temperature and pressure involved in propellant combustion are sufficient to initiate the Thermit reaction.

(U)   Phase III - Studies of Catalysts with Composite Propellants

(U)   After completion of Phase I and Phase II studies, results of the experiments performed were analyzed and interpreted. In the light of the previously accumulated data and results obtained during these phases, a mechanism for the catalysis of burning rate by iron compounds was postulated. In addition, experiments were devised to prove or disprove the validity of the postulated mechanism.

(U)   The basis philosophy behind the technical approach to defining a mechanism for the catalysis of burning rate by iron compounds is as follows:

(U)   1.   Place emphasis on the determination of the effect of iron compounds upon the thermal decomposition of the individual propellant ingredients and their effect upon the interaction of these propellant ingredients.

(U)   2.   Research into a mechanism requires a large number of relatively simple experiments in order to determine the effect of only one variable at a time.

(U)   3.   Experiments were performed, as closely as practically feasible, to conditions which simulate propellant combustion because it is obvious that increased temperature and pressure effect chemical as well as physical interactions.

(U)   4.   It is likewise important to remember that in studies designed toward determining a mechanism, negative results are just as important as positive results. The technical approach was designed, in part, toward the elimination of several theories.

(U)   5.   The catalysts used in this study consisted of iron oxide, freshly sublimed ferrocene, butyl ferrocene[1] (as a liquid derivative of ferrocene), ferrocene carboxylic acid (as the solid derivative) and potassium ferriferrocyanide as a typical ferriferrocyanide. The basic propellant formulation was as follows:

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	Weight, %
PBAA	16.0
Aluminum powder	16.0
Ammonium perchlorate*	68.0

* The ratio of 20-micron to unground material will be 75/25.

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The additives to be incorporated into this formulation were substituted for binder.

(U)   Experiments conducted under these phases, and the results obtained, are discussed in detail herein.

SECTION II

SUMMARY

(U)   The specific objective of this program of applied research was to determine the chemical mechanism by which materials such as iron oxide, ferric ferrocyanide, ferrocene, and ferrocenyl derivatives increase the burning rate of ammonium perchlorate oxidized propellants. The approach pursued by the Huntsville Division of Thiokol Chemical Corporation to determine a burning mechanism was to conduct the following three-phase program: Phase I - Decomposition of Catalysts, Phase II - Decomposition of Catalysts with Propellant Ingredients, and Phase III - Studies of Catalysts with Composite Propellants.

(U)   Experiments designed to determine the role of iron containing catalysts in the decomposition of various propellant ingredients and their effects upon the interaction of these propellant ingredients were conducted under Phase I studies. The interaction, if any, between iron containing catalysts and ammonium perchlorate was studied under Phase II. The experimental data which resulted from these studies were analyzed and interpreted during Phase III and a mechanism for the catalysis of burn rate by iron compounds was postulated. In addition, experiments were conducted to prove or disprove the validity of the postulated mechanism.

(U)   These studies have indicated that the following postulation is one which best accounts for the phenomena encountered in the technology of increasing the burn rate of composite propellants.

(C)   It is known that if the oxidizer deflagration reactions reach equilibrium at 1,000 psi, a temperature of approximately 1200°C could be attained. The burn rate of a given propellant is then dependent upon how near to the equilibrium temperature the oxidizer decomposition reactions approach at a given distance (less than 10 microns) from the regressing surface. The higher the temperature attained very close to the surface, the more the heat feed back to the surface and, therefore, the more rapid the surface regression rate.

(C)   The oxidizer, under the influence of this oxidizer decomposition flame, decomposes initially into perchloric acid and ammonia. The rate of perchloric acid decomposition will then be the rate determining reaction in attaining the equilibrium temperature. The initial decomposition of perchloric acid proceeds via the formation of the hydroxyl and chlorate free radicals. It is believed that this reaction occurs more efficiently upon the surface of an iron oxide particle, resulting in higher temperature generated very close to the surface. As is

the case in any catalytic reaction, there is a leveling off of catalytic effect with increasing sites for catalysis. Such is observed for propellants containing iron oxide.

(C)   Little, if any, effect on burn rate can be attributed to reactions occurring more than 10 microns from the surface. This is evident from the fact that variations in aluminum content (0 to 16 percent) have only a very slight effect upon burn rate. Therefore, flame temperature on the heat of oxidation of aluminum are not rate controlling functions.

(C)   The iron (III) oxide resulting from the very rapid oxidation of ferrocene and other organic iron containing compounds is of extremely small particle size and extraordinarily high specific surface, which accounts for the increased burn rates attainable from the use of these materials. In addition, the heat of oxidation of these compounds serves as a further source of heat to the burning surface. Visual observation of the oxidation of ferrocene reveals a reaction which appears similar to an explosion with expulsion of a multitude of micro-fine iron (III) oxide from the surface. The use of organic iron compounds in composite propellants serves as a source of generation in situ of iron oxide particles, the particle size of which is much smaller than could be satisfactorily processed into a propellant.

(C)   The efficacy of iron compounds in the burning process is, therefore, a means whereby the temperature of the oxidizer flame zone within a few microns of the surface can be increased.

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SECTION III

EXPERIMENTAL ACCOMPLISHMENTS

(U) 1. Phase I - Decomposition of Catalysts

(U)   This phase of effort was concerned with determining the decomposition
(oxidation) products of the materials considered to be catalysts.

(U)   a. Iron Oxide

(U)   The iron oxide most commonly used in composite propellants is an
alpha, rhombrohedral type. Although one would not expect any decomposition
or reaction when this type of iron oxide is heated under pressure in air or
oxygen, such a supposition must be proved.

(C)   Samples of iron (III) oxide were heated to 800°C in air and in atmos-
pheres containing 20 and 30 percent oxygen. Examination of the resultant
material by X-ray diffraction showed that the material was unchanged in
structure. Careful microscopic examination of the surface of individual par-
ticles of Fe_2O_3 revealed no pitting, scratches or other signs of reaction.

(C)   A sample of (516M) α rhombohedral iron (III) oxide was placed in a
Paar oxygen bomb and pressurized to 40 atmospheres with pure oxygen.
Following ignition, the sample was examined by X-ray diffraction (Figure 1).
No change was noted. The experiment was repeated at 200°C with identical
results.

(C)   Another sample of iron (III) oxide was heated to 1600°C in a muffle
furnace. The melting point of iron (III) oxide is 1565°C and it has been
reported that reduction to FeO accompanies melting; however, upon cooling
no trace of the divalent material was detected.

(U)   b. Ferrocene

(U)   Differential thermal analysis (DTA) of pure ferrocene (Figure 2)
revealed two endotherms. The assignment of these peaks to either sublimation,
melting, and boiling had not been previously accomplished.

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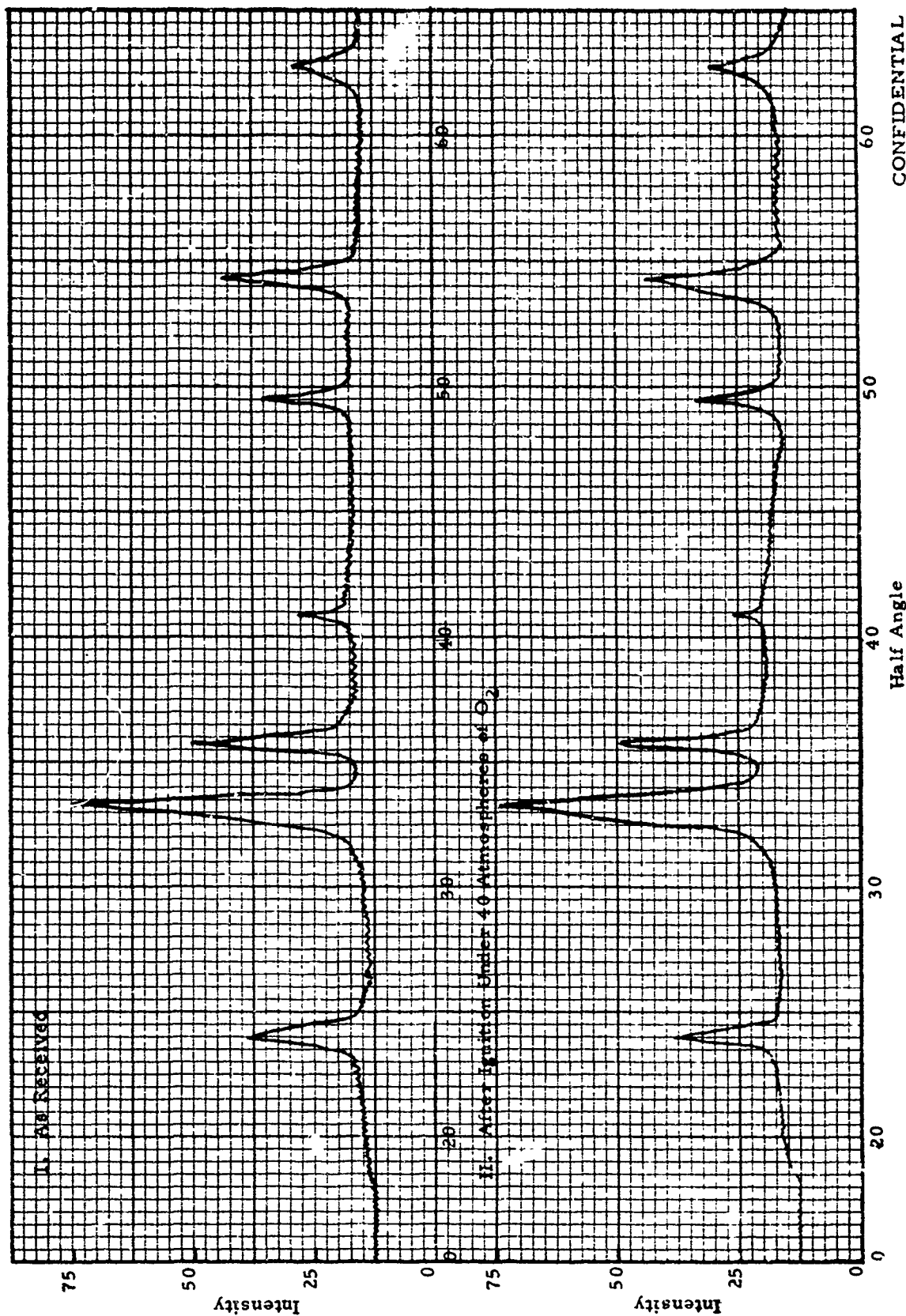
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Figure 1. X-Ray Diffraction Pattern (CuKα) of Fe_2O_3 (516M).

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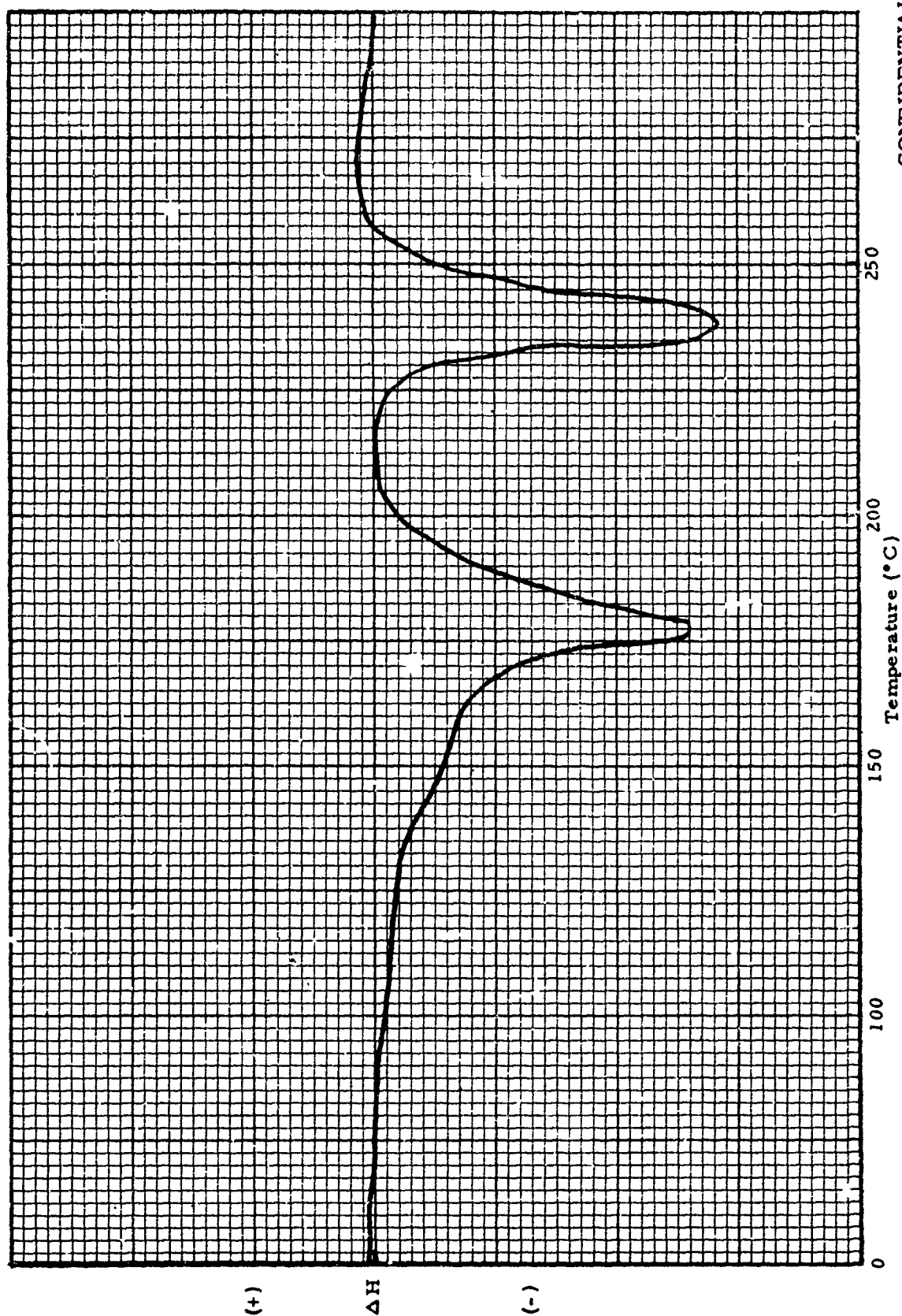
Figure 2. Differential Thermogram of Ferrocene (Heating Rate 10°/Minute).

(C)   Cycling the ferrocene sample between 160 and 185°C revealed that the first endotherm is reversible. This endotherm can be attributed to melting. The reported melting point for ferrocene is 173°C (1)[2]. The latter endotherm, which is not reversible, can then be attributed to boiling. Further proof of the latter assignment can be offered since no decomposition occurred as evidenced by the absence of residue in the DTA tube. The heating rate was 10°/minute; therefore, at heating rates of greater than 10°/minute, it is shown that sublimation is of little concern. The slow decrease in the base line prior to the first endotherm has been shown to be caused by sublimation. Careful microscopic examination of ferrocene being heated at 10°/minute resulted in the observation that noticeable sublimation begins at 90°C. The sublimation does not appear as an endotherm in the differential thermogram simply because of the small surface area exposed in a DTA tube. However, at heating rates attained in conventional composite propellants ($>>>$ 10°/minute) it is probable that neither sublimation nor melting or boiling of ferrocene occur. In view of such high heating rates and the ease of oxidation of ferrocene, it is felt that under the influence of an oxidizer flame zone, ferrocene is immediately oxidized from the solid state to iron (III) oxide.

(C)   Solid, molten, and gaseous ferrocene was burned in air. In each case the resultant residual product was Fe_2O_3 (α rhombohedral) as determined by X-ray diffraction. The particle size of the iron oxide produced in this process is smaller than conventionally utilized iron (III) oxide.

(C)   A sample of freshly sublimed ferrocene was burned in a Paar oxygen bomb under 20 atmospheres of oxygen. The resultant product was an extremely fine, powdered material, red-brown in color and strongly resembling iron (III) oxide. The gaseous products were water and carbon dioxide. Confirmation of the presence of Fe_2O_3 by X-ray diffraction was not clear cut. The initial pattern revealed very small broad peaks and although there existed peaks attributable to crystalline iron (III) oxide and iron (III) oxide hydrate, it was presumed that the majority of the product was amorphous iron (III) oxide. The material was heated for several hours at 600°C and the X-ray pattern was somewhat more definitive. The peaks attributable to iron (III) oxide were slightly more intense but the major portion of the material still appeared to be amorphous. The experiment was repeated at 80°C. No indication of product change was noted, although the amount of crystalline iron (III) oxide seemed to increase slightly. However, this observation is within experimental error.

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2. Numbers in parenthesis indicate references which may be found at the end of this report.

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(U)   It is difficult to visualize the formation of an amorphous material from the oxidation of ferrocene in the presence of excess oxygen. Therefore, the possibility that the particles of Fe_2O_3 formed are for the most part too small to diffract X-ray was investigated.

(C)   In discussions with Dr. A. F. Wells of I. C. I., Manchester, England it was pointed out that particles of a size less than approximately 1000 Å (0.1 micron) are too small to provide a meaningful diffraction pattern. Closer observation of the particles resulting from the oxidation of ferrocene revealed that these crystals may indeed be that small. Comparison under a microscope of these particles with iron (III) oxide of 200 Å particle size shows that much of the material resulting from the oxidation of ferrocene has a particle size between 200 and 1000 Å. Samples of the oxidation product submitted for elemental analysis confirmed that the product was indeed iron (III) oxide.

(U)   A mixture of 10 percent ferrocene and 90 percent ammonium perchlorate was subjected to DTA. In such an oxidizing atmosphere, a determination of whether, under slow heating rates, ferrocene would totally sublime before decomposition of the oxidizer began was desired. In addition, an explanation of the early exotherm observed with mixtures of ammonium perchlorate (Figure 3) and ferrocene or ferrocene derivatives was needed.

(C)   The DTA was terminated at 220 to 240°C, just beyond that point of the observed exotherms. Upon removal of the tube, it was observed that considerable ferrocene had sublimed to the top of the tube and the undecomposed ammonium perchlorate was completely covered with a grey-black coating. X-ray diffraction of the coated oxidizer revealed only peaks corresponding to ammonium perchlorate. Subsequent grinding of the coated oxidizer, followed by leaching the oxidizer out by methanol extraction, resulted in an extremely finely divided black material. No X-ray pattern was obtainable from this material. The black substance was insoluble in water and a variety of organic solvents (benzene, diglyme, dimethylformamide, carbon tetrachloride and chloroform). This sample was not large enough for an elemental analysis. In order to identify this material, larger samples were prepared. The aforementioned mixture was repeated, pulverized in a mortar and pestle, and extracted with methanol until free from ammonium perchlorate. This process did not change the color of the coating material. Very careful X-ray examination revealed the material to be, for the most part, finely divided iron (III) oxide. No indication of unreacted ferrocene was obtained. The black color of the residue has been attributed to unoxidized organic moieties, since heating of the residue in a muffle furnace (600°C) for ten minutes resulted in the characteristic red-brown color of iron (III) oxide.
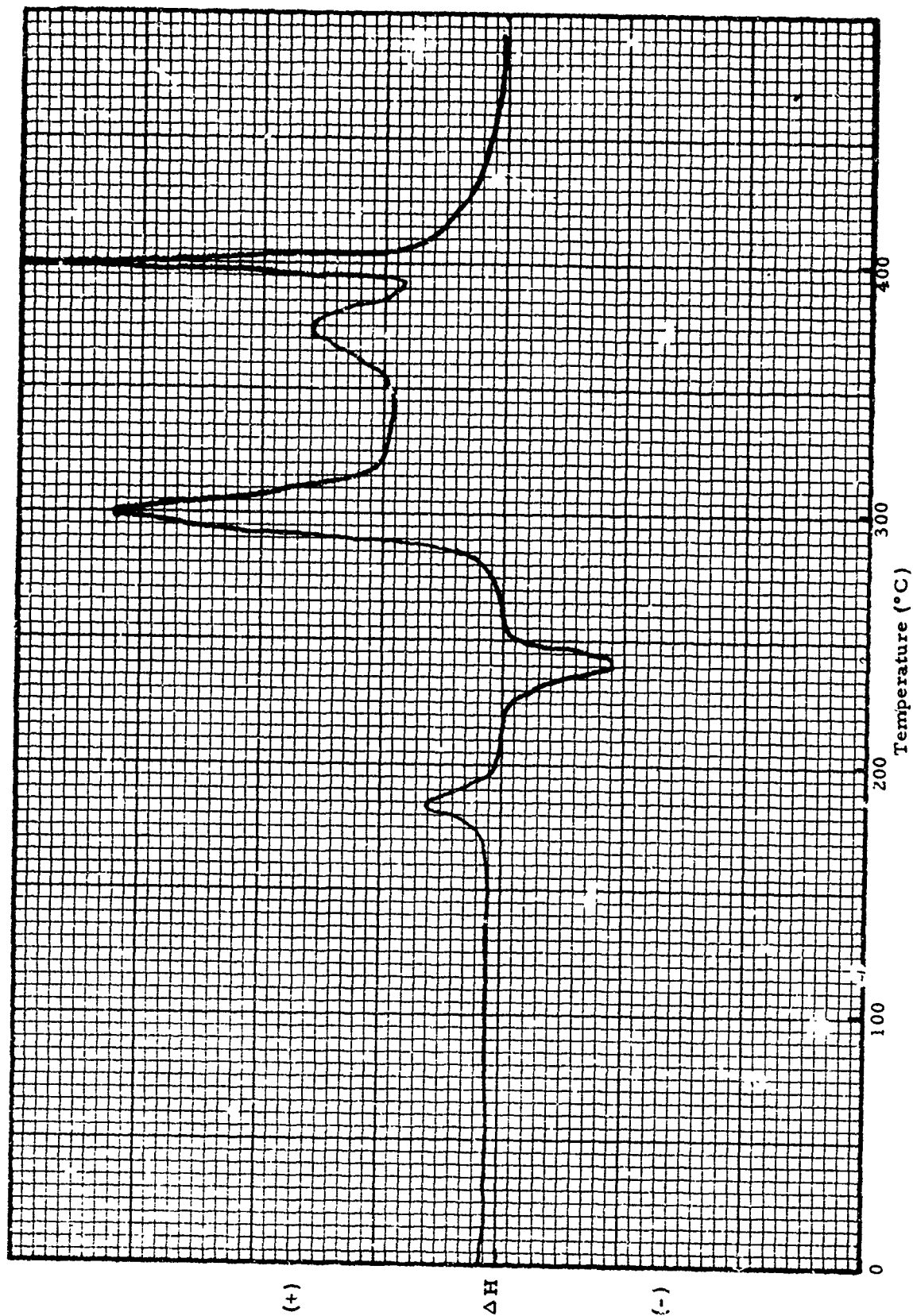
Figure 3. Differential Thermogram of a Mixture of AP (95) and Ferrocene (5) (Heating Rate 10°/Minute).

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(U)   c.   n-Butyl Ferrocene

(C)   Butyl ferrocene was burned in air and iron (III) oxide was the sole resulting product, after elimination of the carbon ash by a brief heating period at 700°C.

(C)   Butyl ferrocene was burned in a Paar oxygen bomb under 20 atmospheres of oxygen. The resultant product was a finely divided red-brown powder very similar to that obtained from the combustion of ferrocene. The X-ray diffraction pattern was ill-defined although small broad peaks were noted which corresponded to iron (III) oxide and iron (III) oxide hydrate. It should be noted that a slightly larger amount of crystalline iron (III) oxide was present in the sample from the combustion of butyl ferrocene than that from ferrocene. Further improvement in the X-ray pattern resulted from the combustion of butyl ferrocene under 30 atmospheres of oxygen.

(C)   As in the case of ferrocene, it was shown that the resultant material from the combustion of buryl ferrocene is submicron in particle size and may be too small for proper identification by X-ray diffraction techniques. No explanation is given for the fact that better X-ray patterns are obtained from the oxidation product of butyl ferrocene than that of ferrocene.

(C)   Thermogravimetric weight loss studies of butyl ferrocene at 200, 300, and 400°F in air show only volatilization with very slight decomposition. The degree of decomposition was less than 2 percent at 400°F; the decomposition product was a black tar. In 1964, several months work at Thiokol - Huntsville Division was directed toward determining the air oxidation product of butyl ferrocene. It was found that the product contained carbon, hydrogen, oxygen, and iron with the formula $C_{12}H_{15}FeO_5$; however, the structure could not be determined. The material resulting from this experiment is the same organic tar.

(U)   d.   Prussian Blue (Potassium Ferriferrocyanides)

(C)   Prussian Blue ($KFe[Fe(CN)_6] \cdot x\ H_2O$) was heated in air at 400°C for two hours. The main gaseous decomposition product was cyanogen (C_2N_2) and the resultant residue consisted of iron (III) oxide (α rhombohedral) and potassium chloride. The alkali chloride is a standard impurity in Prussian Blue. Another sample was heated in air at 600°C and the gaseous product was mainly nitrogen. However, the residue was the same as obtained at the lower temperature. The difference in gaseous decomposition products at the two temperatures has been previously reported (2).

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(C) Combustion of Prussian Blue under 20 atmospheres of oxygen was accomplished. The residue obtained from the oxidation was the same as observed in similar experiments with ferrocene and butyl ferrocene. The X-ray diffraction analysis again was difficult because of extremely small particles. However, the presence of iron (III) oxide and iron (III) oxide hydrate was confirmed.

(U) e. High Pressure Studies

(U) In order to more closely simulate propellant deflagration conditions, differential thermograms were obtained at 200 psia for the respective catalysts. Naturally, no decomposition of iron (III) oxide was noted.

(C) A DTA of ferrocene at 200 psig revealed no unexpected occurrences. The melting point at 174 to 180°C was unchanged from atmospheric pressure runs; however, as may be seen on Figure 4, the boiling point was extended from 237°C out to 437°C. This observation is a further indication that sublimation or boiling of ferrocene is of no significance in a burning mechanism. Oxidation will certainly occur before volatilization.

(C) The DTA of butyl ferrocene at 200 psig is straightforward. No exothermic reaction occurs under the nitrogen atmosphere. The boiling point of butyl ferrocene at 200 psig was 465°C (Figure 5).

(U) 2. Phase II - Effect of Catalyst Upon Propellant Ingredient Decomposition

(U) a. Task A - Iron Catalysts Effects of Ammonium Perchlorate
              Decomposition

(U) This phase of the program is designed to study the interaction, if any, between iron containing catalysts and ammonium perchlorate.

(U) Bircumshaw and Newman (3) have proposed that the effectiveness of catalysts such as iron (III) oxide may be ascribed to the ease with which they can act as a bridge in the electron transfer reaction which supposedly occurs in the low temperature decomposition of ammonium perchlorate as follows:
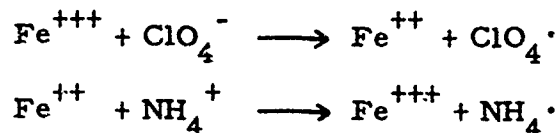
$$Fe^{+++} + ClO_4^- \longrightarrow Fe^{++} + ClO_4 \cdot$$

$$Fe^{++} + NH_4^+ \longrightarrow Fe^{+++} + NH_4 \cdot$$

14
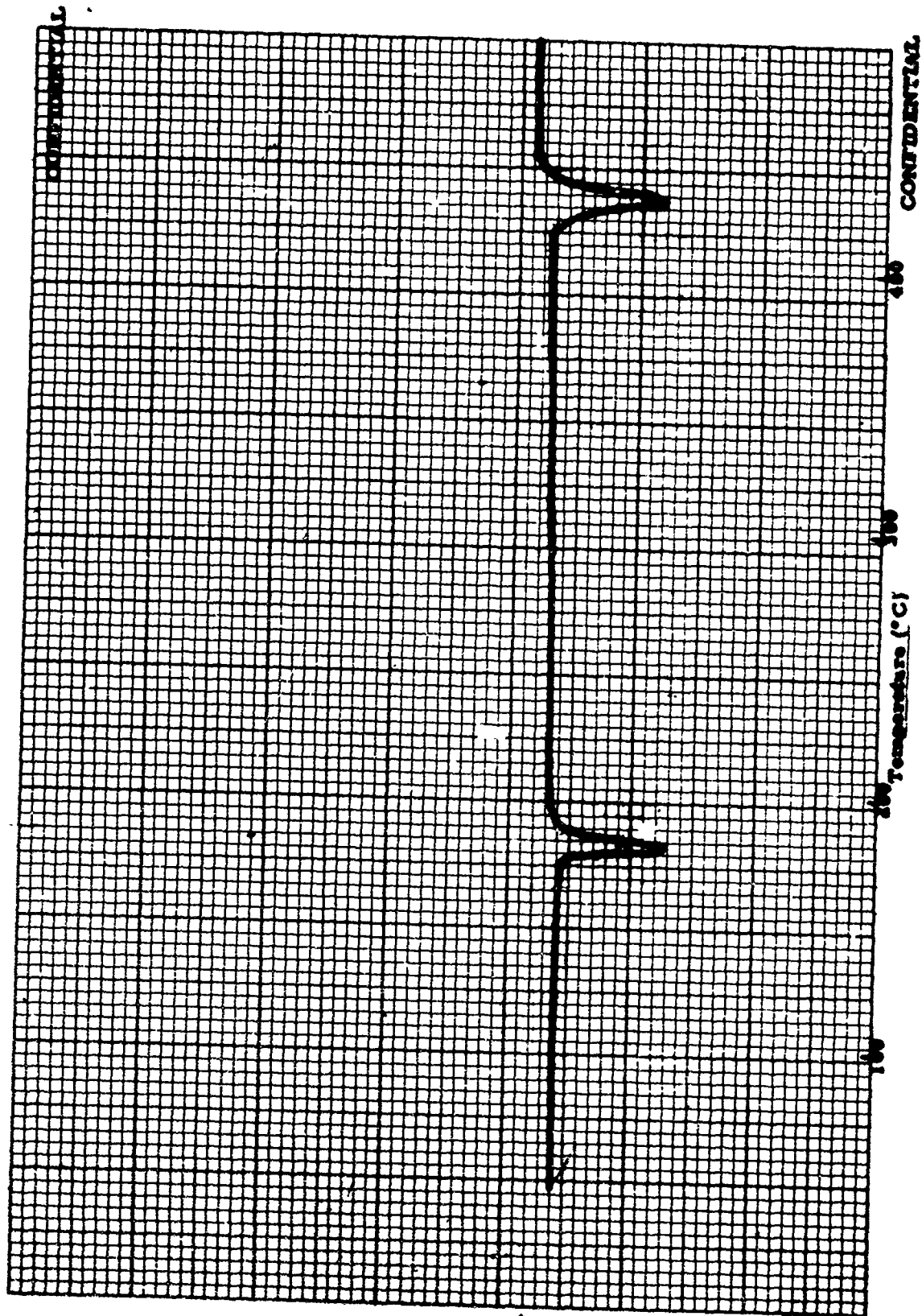
Figure 4. DTA of Ferrocene Under 200 psig N$_2$.
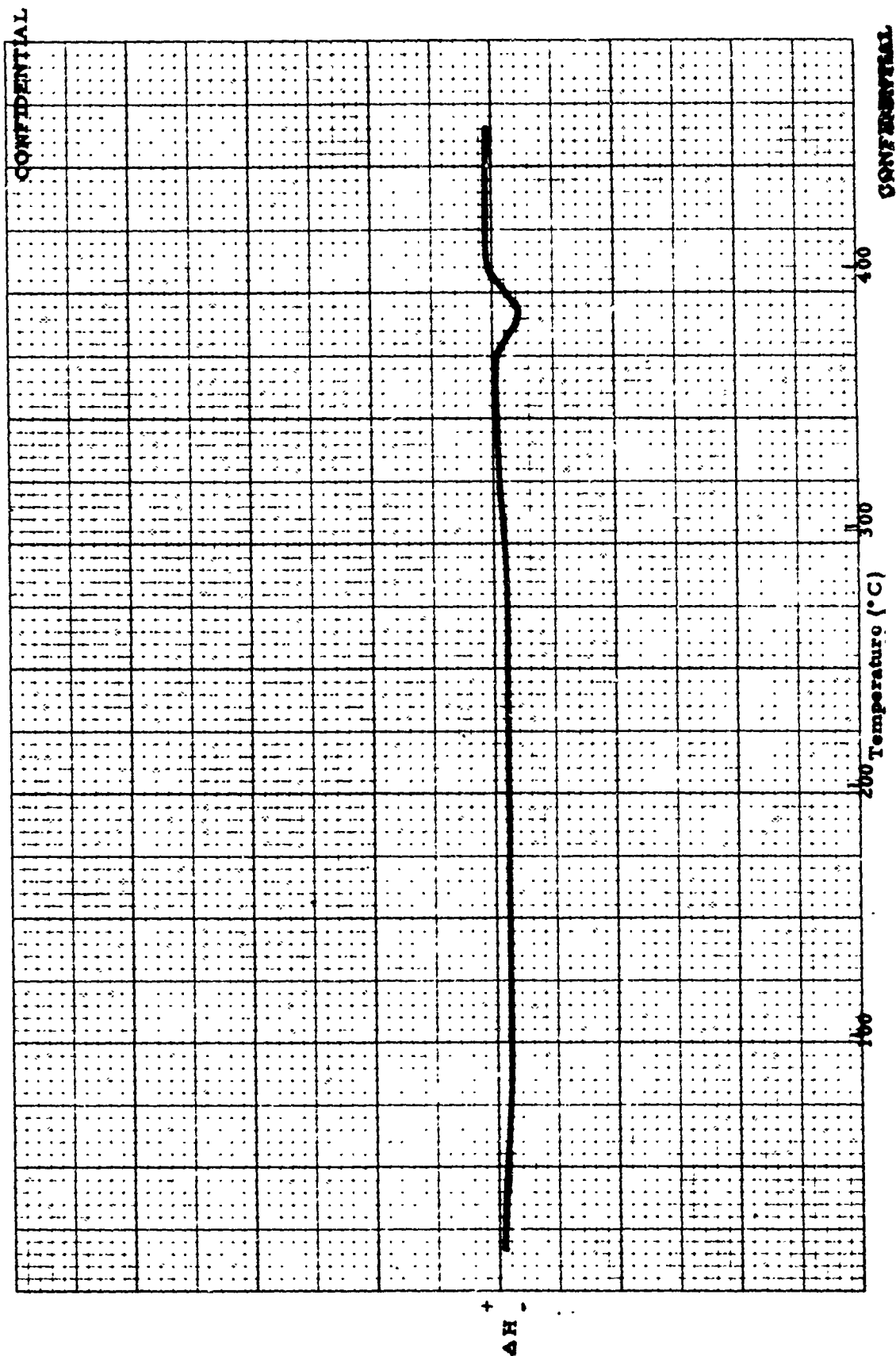
Figure 5. DTA of Butyl Ferrocene Under 200 psig N_2.

(U)   The proposition that iron compounds can possibly form complexes with ammonia at high temperatures, thus providing the anhydrous perchloric acid more time to decompose, is presently favored by J. E. Land (4).

(U)   The fact that iron compounds are noted for their ability to facilitate free radical formation is the basis of a third theory. The rate controlling step in the decomposition of perchloric acid has been shown to be the formation of hydroxyl and chlorate free radicals (5, 6). Therefore, it seems feasible that when perchloric acid comes in contact with an iron oxide particle, the rate of decomposition of $HClO_4$ into free radicals might be enhanced.

(U)   The experiments in this phase of work were designed to test these postulates under a variety of conditions in order to determine which was most correct.

(U)   (1)   Electron Transfer Studies (Solid Phase Interaction)

(U)   (a)   Interaction of Iron (III) Oxide and Ammonium Perchlorate

(U)   The first series of experiments in this area were designed to visually examine possible interactions between ammonium perchlorate and iron containing catalysts under conditions of close proximity and slowly increasing temperature. Examination by photomicrography, X-ray diffraction and elemental analysis revealed the changes that took place.

(C)   A particle of iron (III) oxide was placed in intimate contact with a particle of ammonium perchlorate. Heat was slowly applied (1°C/2 seconds). The resultant decomposition was examined under a high powered microscope and then repeated. Color photomicrographs were taken at points of interest. At 170°C, a white glaze (opaque) appeared on the surface of the ammonium perchlorate. This is the first point of noticeable sublimation of the oxidizer. The volume increase associated with the phase transition of ammonium perchlorate was perceptible at 240°C and at this point, small amounts of subliming oxidizer condensed on a cold plate held 1 inch above the reactants. The oxidizer particles continued to sublime, for the most part irreversibly, until a temperature of 340 to 360°C was obtained. The residue from the oxidizer decomposition appeared as small string-like shells which were extremely frangible and amounted to approximately 1 to 5 percent of the original weight.

(C)   The particles of iron oxide that were originally in contact with several of the oxidizer particles remained on the string-like shells and in the same relative position as formerly occupied. The iron oxide did not change color during the experiment, nor did the ammonium perchlorate particles sublime more rapidly at the contact point between the particles of ammonium perchlorate and iron oxide. In fact, particles of ammonium perchlorate far removed from the particles of iron (III) oxide sublimed at the same approximate rate as the

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particles in intimate contact with the iron oxide. Also, the contact point between the particles of iron oxide and ammonium perchlorate was maintained throughout the ammonium perchlorate sublimation (Figure 6). In fact, it would appear that the iron oxide serves as a heat sink resulting in little, if any, decomposition of the oxidizer at the contact point between the oxidizer and iron oxide.

(C)   One interesting observation made during these studies was that pure sublimed ammonium perchlorate could be collected on a cold plate held 1 inch above the decomposing oxidizer. Although the amount of material obtainable is small in comparison to the starting amount, this observation tends to indicate that the sublimation of ammonium perchlorate is not as irreversible as once was thought. It should be pointed out that under conditions of burning propellant the sublimation would be quite irreversible.

(C)   The aforementioned experiments were run several times in order to possibly eliminate spurious observations, and photomicrographs were taken each time. It must be concluded that iron (III) oxide is not a catalyst for the solid phase decomposition of ammonium perchlorate. Its efficacy most probably can be attributed to gas phase catalysis of the decomposition of either ammonia or perchloric acid.

(C)   The previous experiment was repeated using ammonium perchlorate that contained occluded iron oxide. Identical results were obtained. The condensed sublimate, which appeared at approximately 220°C, had a slight red-yellow discoloration. A sensitive spot test for iron (utilizing ortho-phenanthroline) indicated that none was present. X-ray analysis indicated that the condensate was pure ammonium perchlorate.

(C)   A mixture of ammonium perchlorate and iron oxide was heated for 2 hours at 200°C. The remaining ammonium perchlorate was extracted with methanol and the iron oxide examined by X-ray. No other compounds were present. The resultant iron (III) oxide was analyzed for the presence of iron (II) compounds by dissolution in HCl, followed by titration with dichromate. No iron (II) was present. The experiment was repeated at 250, 300, and 350°C. No evidence of chemical interaction could be detected.

(U)   (b) Ferrocene - Ammonium Perchlorate Interaction

(C)   Particles of ammonium perchlorate and ferrocene in intimate contact were heated as previously discussed. Sublimation of ferrocene was noticeable at 90°C. Rapid sublimation occurred immediately afterwards. The color of the ammonium perchlorate particles became metallic grey in the 175 to 185°C range in temperature. The crystals became light orange to pink at 300°C.

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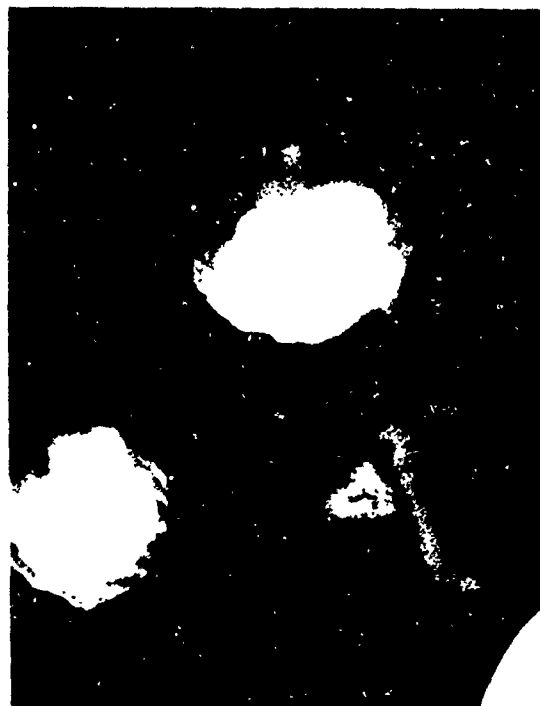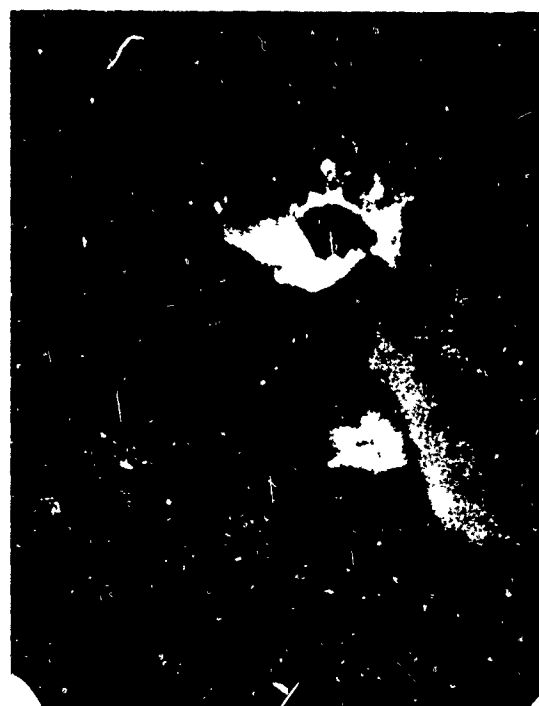
Figure 6. Decomposition of Ammonium Perchlorate in Contact with Fe_2O_3

(Heating Rate – 0.5°C/Minute)

The interior color of the ammonium perchlorate particles became white at 320°C, with noticeable orange and brown streaks on the surface of the particles. A small, dark brown residue remained where each particle of ferrocene had originally been positioned. This dark brown residue from ferrocene sublimation was of some interest. Additional residue was obtained and examined by X-ray. A strong and unidentified peak was obtained at 31.6 to 31.8° half angle. X-ray analyses of crystals of ferrocene, pulverized ferrocene, and ferrocene from the   t that was condensed on a cold plate did not reveal the peak (31.6°\   ' :d from the residue of sublimed ferrocene. It was assumed, ther'   t this residue must be a decomposition product of ferrocene.

(C)   ... .s interesting to note that at slow heating rates such as occur in these experiments, the majority of the ferrocene sublimes before 100°C; however, at 175 to 180°C (the melting point of ferrocene) the oxidizer crystals turn steel grey and black. The color then disappears near the boiling point of ferrocene and only streaks of red and yellow appear on the oxidizer crystal when rapid decomposition sets in. It is possible that some of the ferrocene sublimes into the cracks and crevices on the oxidizer crystal and at the melting point spreads over the crystal. There is some evidence at this point that the ferrocene has partially decomposed because the X-ray pattern of the grey-black residue revealed no crystallinity. It is assumed that the red and yellow streaks observed at higher temperatures is an oxidation product of ferrocene, most probably, iron (III) oxide.

(C)   Another possibility to explain the sequence of events observed in this experiment is that as the ferrocene sublimes into the cracks and crevices of the oxidizer crystal, the oxidizer begins to decompose and in the presence of the oxidizing atmospheres the ferrocene is either partially or completely oxidized to Fe_2O_3. The oxide could then react with the HCl, a final product of the oxidizer decomposition, to form $FeCl_3$. The color changes observed on further heating correspond closely to the melting point and boiling point of ferric chloride. The yellow-red streaks that remain on the crystal could then be traces of iron (III) oxide formed from the thermal decomposition of some hydrated ferric chloride that may have been present on the surface.

(C)   A large residue was obtained by repeating the above mentioned experiment. The residue was pulverized in a mortar and pestle and extracted with methanol until free from ammonium perchlorate. X-ray examination revealed the material to be, for the most part, finely divided iron (III) oxide. No indication of unreacted ferrocene was obtained. The black color of the residue has been attributed to unoxidized organic moieties, since heating of the residue in a muffle furnace (600°C) for 10 minutes resulted in the characteristic red-brown color of iron (III) oxide.

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(U)   (c) Butyl Ferrocene - Ammonium Perchlorate Interaction

(C)   Particles of ammonium perchlorate were coated with butyl ferrocene
and the same experiment repeated. Volatilization of butyl ferrocene seemed
to be complete at 180°C, resulting in a red-brown residue deposited at
scattered points over the oxidizer surface. X-ray diffraction studies showed
that after oxidizer decomposition was complete, this red-brown residue was
iron (III) oxide. The particles were so finely divided on the surface that the
over-all appearance of the crystal was metallic grey to ebony in color. The
oxidizer crystal surface turned a light orange-pink color at 290°C and from
pink to white at 310°C. Red and orange color was retained in localized con-
centrations on the exterior shell of the ammonium perchlorate particles.
No explanation is available for the fact that iron (III) oxide could be detected
on the surface of ammonium perchlorate at the conclusion of the decomposition
with butyl ferrocene, and not detected with ferrocene. However, the results
of the two experiments are very similar and it is concluded that at low heating
rates, both ferrocene and butyl ferrocene are volatilized before substantial
oxidizer decomposition begins.

(U)   (d) Differential Thermal Analysis - Thermogravimetric
                            Analysis

(C)   The differential thermogram of "as received" ammonium perchlorate
revealed an exotherm at 300°C ± 20°C. Repeated crystallization of the
ammonium perchlorate from water will greatly reduce the intensity of this
exotherm; in fact, if care is taken in the recrystallization process, the peak
shown on Figure 7 can be nearly eliminated. As may be seen on Figure 8, the
presence of iron (III) oxide mixed with ammonium perchlorate results in a
dramatic increase of the exotherm in question. Attempts to determine the
activation energy for the decomposition associated with the first exotherm
have been unsuccessful. Although values for activation energies have been
measured for this process both with and without catalyst, these values have
been rendered meaningless by variations in the measurements resulting from
slight differences in oxidizer particle size, water content of the oxidizer, and
purity of the oxidizer.

(C)   Thermogravimetric analysis (TGA) of ammonium perchlorate alone
and in mixtures with iron (III) oxide were run. As shown on Figure 9 (Curve 1),
ammonium perchlorate alone revealed a two-phase sigmodial weight loss curve.
Initial noticeable decomposition began at approximately 300°C and after about
10 percent weight loss, the rate of decomposition decreased. At 425 to 450°C,
more rapid decomposition ensued until the sample had totally decomposed.
Addition of 5 percent iron (III) oxide to the oxidizer sample resulted in a single-
phase decomposition which was initiated at approximately 290 to 300°C (Figure
9, Curve 2). In other words, after oxidizer decomposition began, the presence

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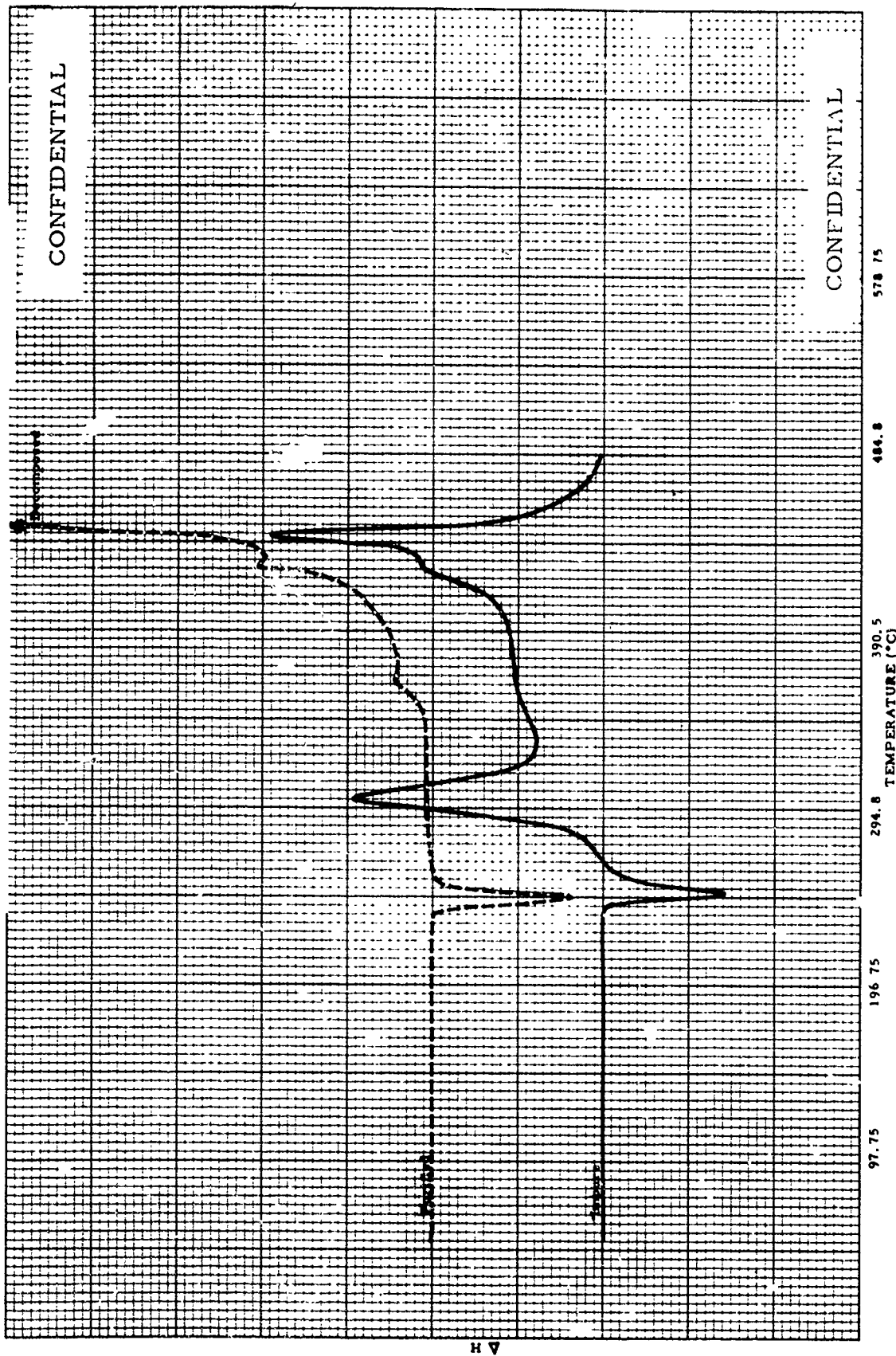
Figure 7. Differential Thermogram of NH_4ClO_4 (Impure vs. Purified).
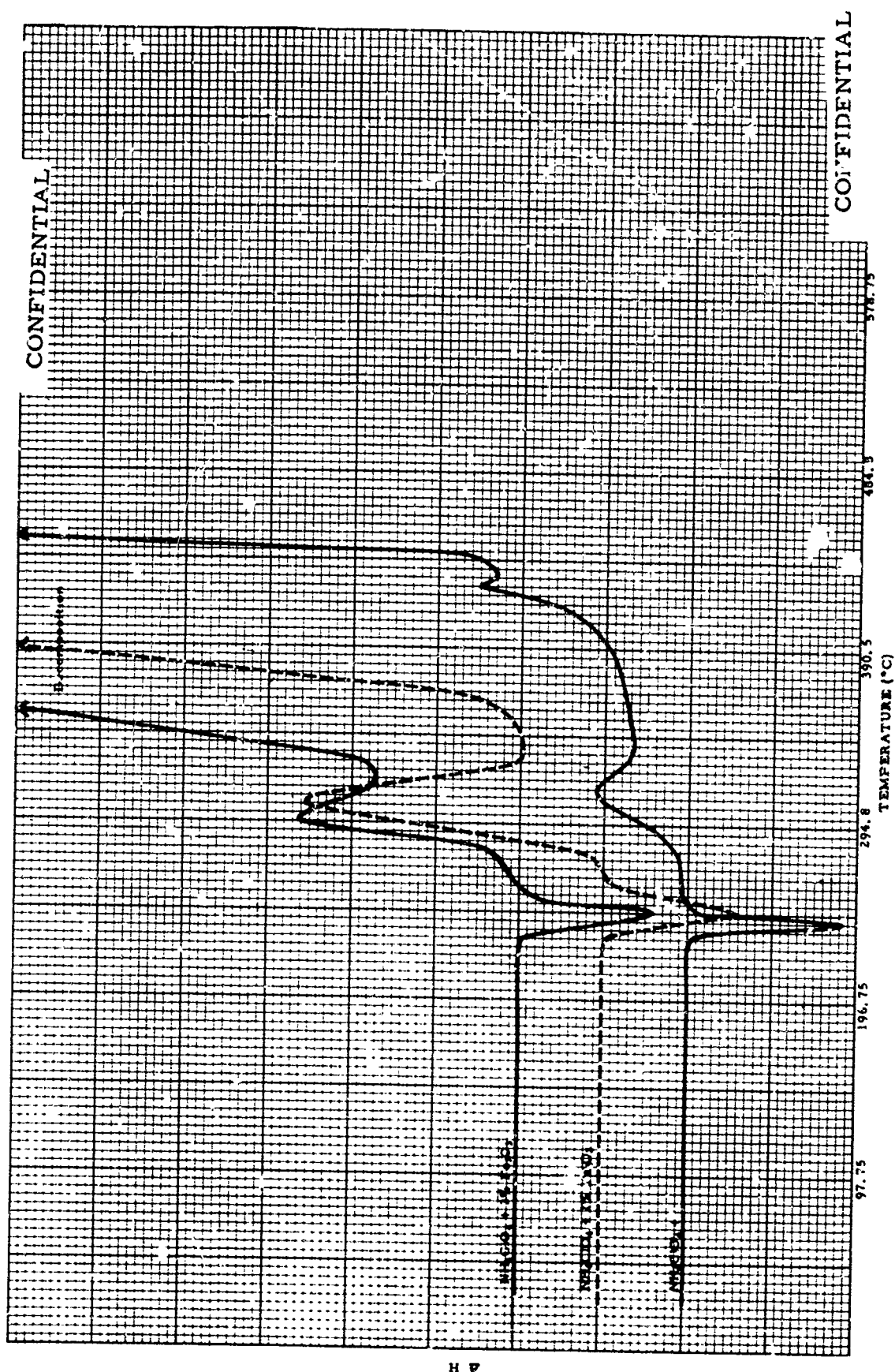
Figure 8. Differential Thermogram of NH_4ClO_4 and Catalysts.
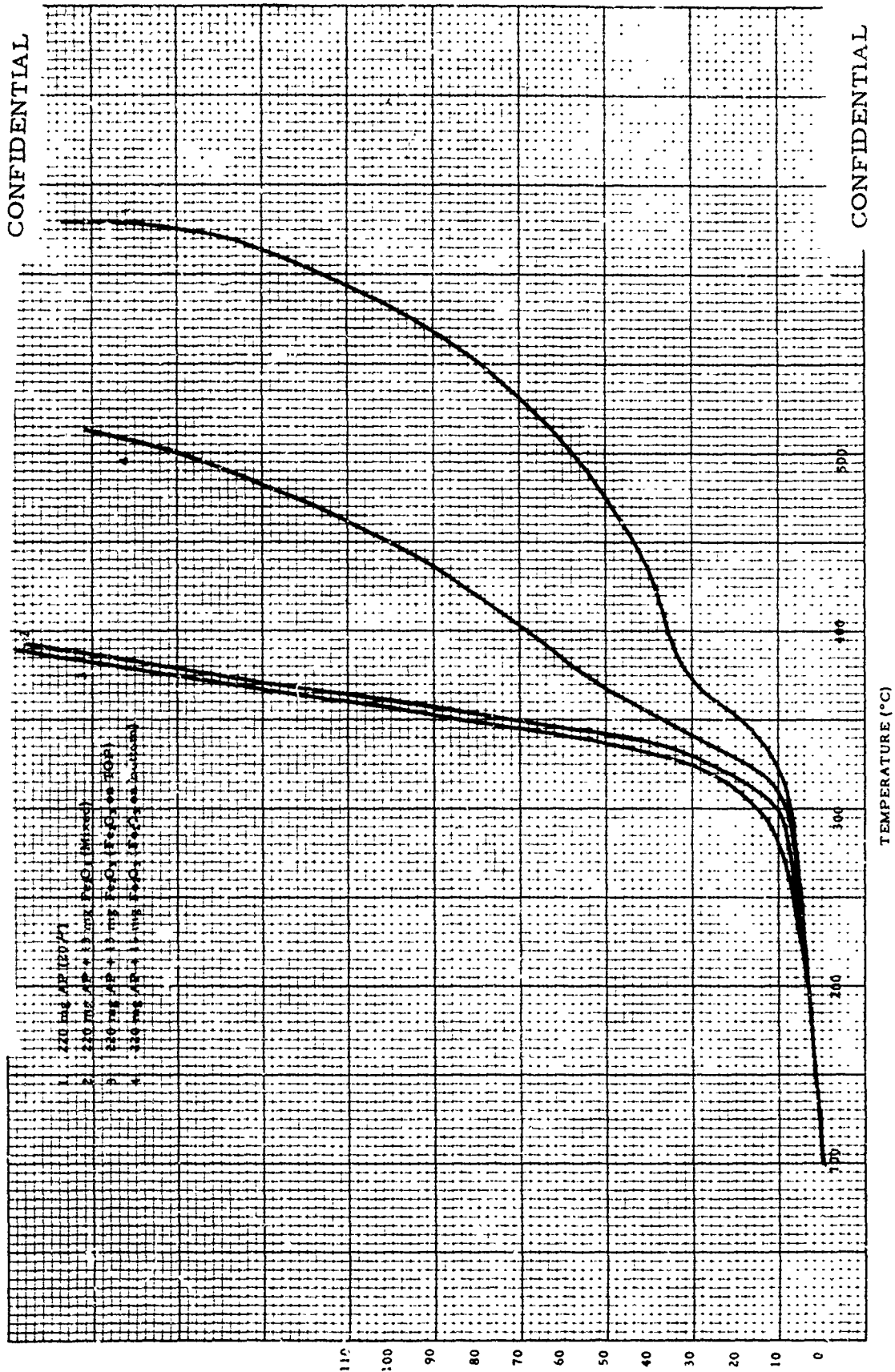
Figure 9. Thermogravimetric Analyses of Mixtures of Iron Oxide and NH_4ClO_4.

of iron oxide effects a total rapid decomposition during the so-called low temperature phase of the oxidizer decomposition.

(C)   In another experiment, the 5 percent iron oxide was simply sprinkled on the top of the oxidizer sample. The resulting TGA revealed that slightly faster oxidizer decomposition occurred (Figure 9, Curve 3) than was the case with the intimate mixture of oxidizer and catalyst. This result points strongly to the fact that iron (III) oxide does not affect the solid phase decomposition of ammonium perchlorate but catalyzes gas phase reactions close to the surface resulting in more heat which, in turn, increases the rate of solid phase decomposition.

(C)   Another experiment, in which the 5 percent iron oxide was added to the crucible first and then covered with ammonium perchlorate, resulted in intermediate behavior between the decomposition of pure ammonium perchlorate and premixed iron oxide and ammonium perchlorate. The decomposition began at 295°C (Figure 9, Curve 4), but was less rapid than that observed with pure ammonium perchlorate. This result, as well as the observation that the oxidizer decomposed initially from the bottom of the crucible, tends again to indicate that the gas phase reaction catalysis is primarily responsible for the increased decomposition rate.

(C)   The DTA of mixtures of ammonium perchlorate and ferrocene is similar to that of mixtures of ammonium perchlorate and iron (III) oxide (Figure 10). There are two differences existing in the DTA of ferrocene and ammonium perchlorate when compared to Fe_2O_3 and ammonium perchlorate; an endotherm at 178 to 186°C, which can be attributed to the melting point of ferrocene, and a slight exotherm at 190 to 230°C, which has been attributed to the oxidation of the molten ferrocene. It should be pointed out that considerable loss in the original weight of ferrocene in the sample occurred between 90 and 120°C, due to sublimation.

(C)   The TGA experiments performed with iron (III) oxide and ammonium perchlorate were repeated using a mixture of 5 percent ferrocene and 90 percent ammonium perchlorate (mixed; Figure 11, Curve 1) and one in which the ferrocene was sprinkled on top of the oxidizer (Figure 11, Curve 2). In both cases, volatilization of ferrocene was noted between 90 and 200°C. No measurable oxidizer decomposition occurred in this temperature range. As was expected, the sample containing the ferrocene on top of the oxidizer lost weight more rapidly. The resultant oxidizer decomposition curve is double-phase sigmodial in nature and similar to that for pure ammonium perchlorate. The exception to this similarity is that the rates of decomposition observed in each phase are more rapid than those for pure ammonium perchlorate. This can probably be attributed to the small amount of ferrocene which was oxidized to iron (III) oxide before it volatilized.
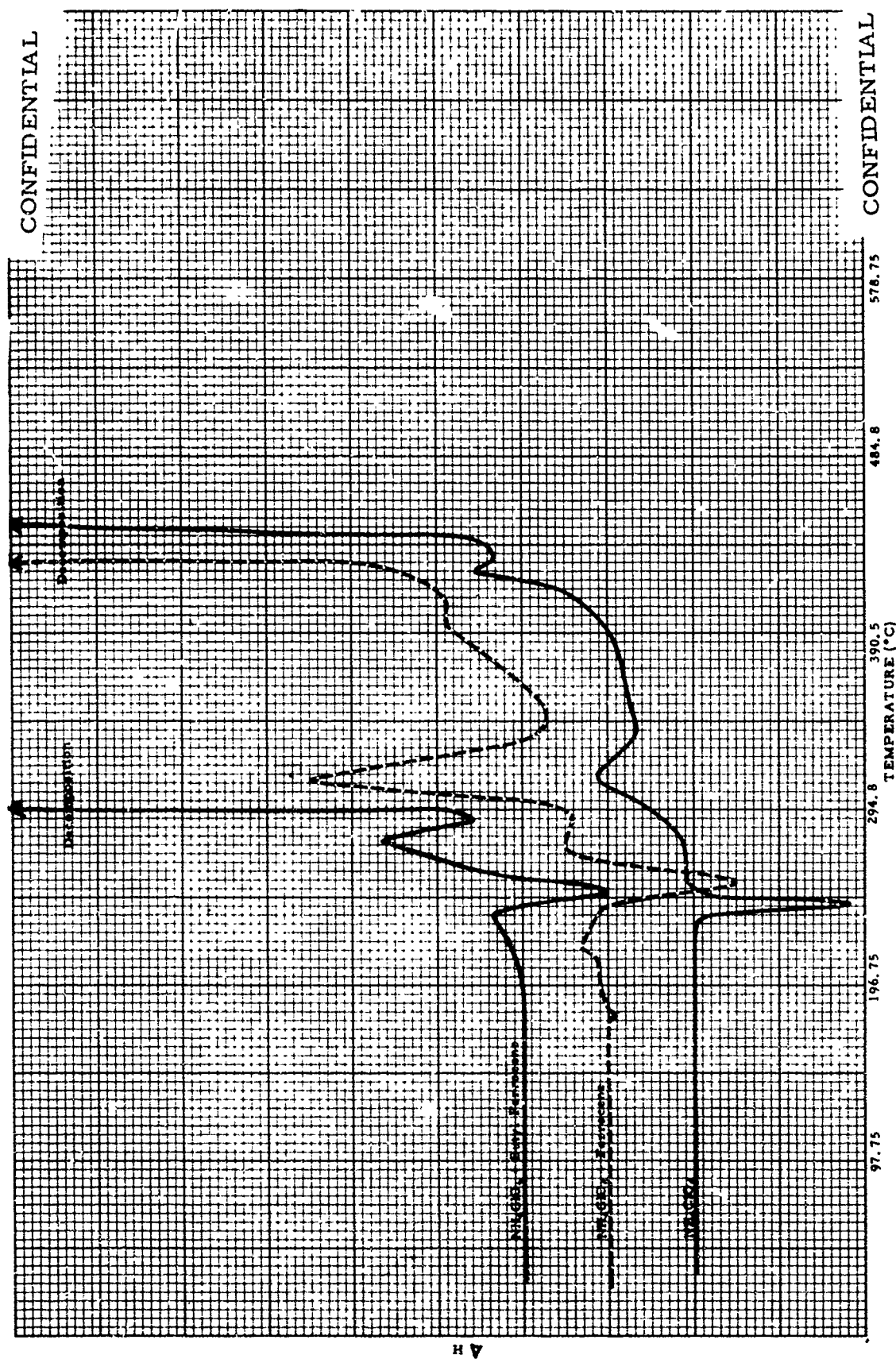
Figure 10. Differential Thermogram of NH_4ClO_4 and Catalysts.
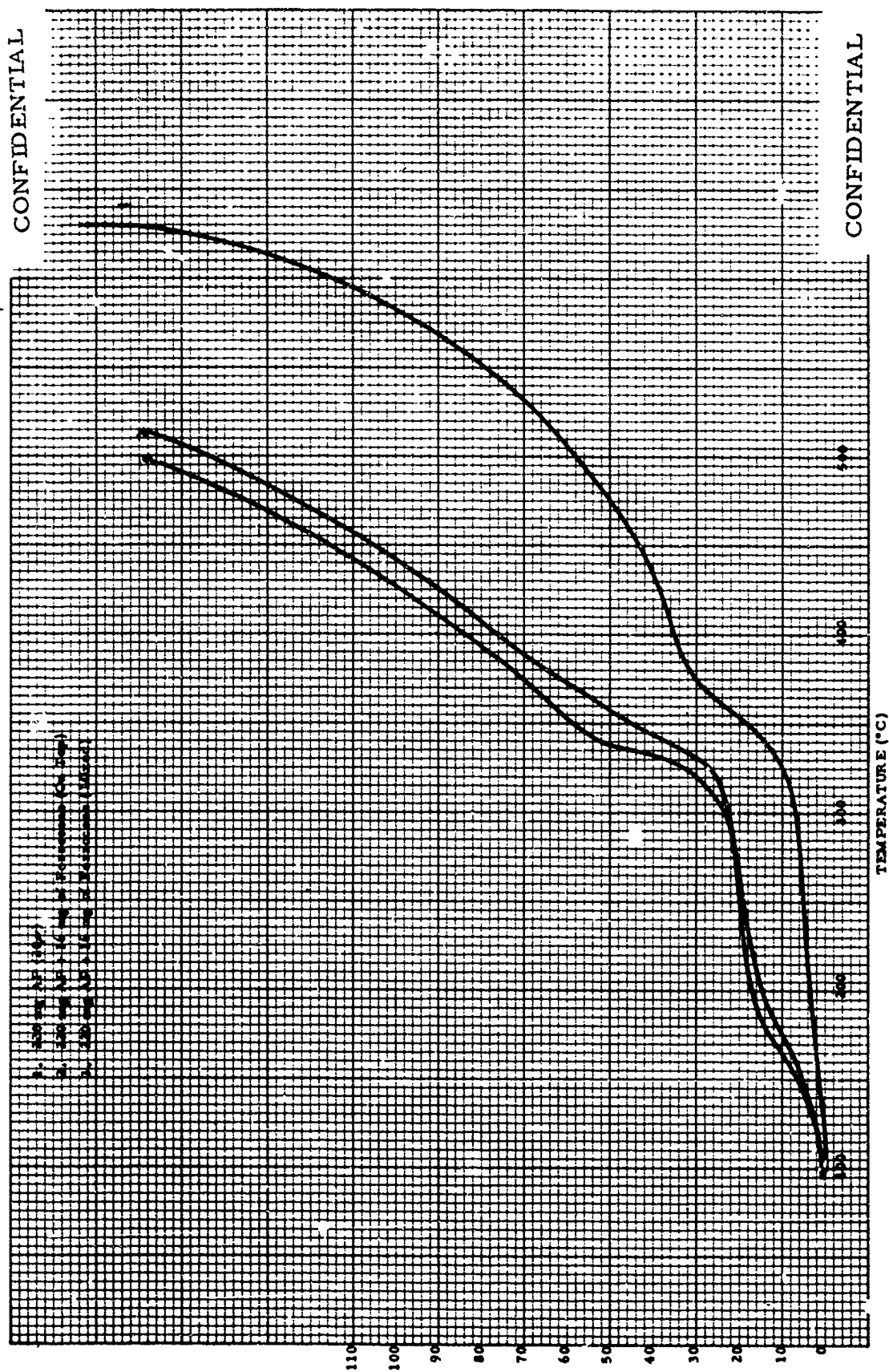
Figure 11. Thermogravimetric Analyses of Mixtures of Ferrocene and Ammonium Perchlorate.

(C)   A series of DTA's and constant temperature TGA's were run on
ammonium perchlorate in order to determine the origin of the first exotherm
in the DTA of ammonium perchlorate. It should be pointed out that the first
weight loss phase in the TGA corresponds in temperature to the first exotherm
in the DTA.

(U)   Essentially, the results of this series of experiments are as follows.

(C)   The first-phase (low temperature) decomposition occurred in the
temperature range of 300 to 400°C. Therefore, several constant temperature
TGA's were run at 340°C (Figure 12). In all cases, the weight loss amounted
to 9.5 to 10 percent of the sample weight.

(C)   It is known that at 240°C the phase change of ammonium perchlorate
from orthorhombic to cubic involves a 9.7 percent volume increase and
resultant density decrease. (No weight loss is associated with this process.)
Therefore, it was decided to investigate whether the approximate weight loss
of 9.5 to 10 percent was coincidental with the phase change or could in some
way be related to, or be a result of this crystalline transformation. A TGA
was run at 340°C until the material showed no more weight loss in 15 minutes.
The loss in weight amounted to approximately 10 percent. The sample was
cooled to 280°C and held at this temperature for 30 minutes. The temperature
was raised to 340°C again and no significant decomposition occurred after 30
minutes. The sample was then cooled to 220°C (below the point of crystalline
transformation) and held at this temperature for 30 minutes. Upon heating
to 340°C again, decomposition occurred readily; however, in no case did the
resultant decomposition result in more than a 10 percent weight loss. The
sample was cycled between 340 and 220°C several times and each time de-
composition occurred at the higher temperature. The amount of weight loss
each time was not constant (varying between 4 and 10 percent). Exposure
time to the lower temperature (220°C) could be a factor in this variance.

(C)   Although the mechanism of this initial 10 pe cent decomposition is
somewhat unclear, it appears that the crystalline transformation at 240°C
from orthorhombic to cubic may indeed be a factor in the initial decomposition
of ammonium perchlorate.

(C)   Constant temperature TGA's at 380°C revealed unusual results. The
initial decomposition ($\sim$ 10 percent) was quite rapid and was followed by
her slower decomposition reaction which ceased after an over-all weight
loss of 30 percent had occurred (Figure 13). The cessation of the decomposi-
tion at 30 percent has been reported several times (7). However, the two-
phase low temperature decomposition was not noted. Heating rates in a TGA
must be extremely slow in order to detect the differences in the activation
energies of these two processes.

(C)   At temperatures above 400°C, all three decomposition phases can be
detected and the final decomposition is acceleratory throughout .
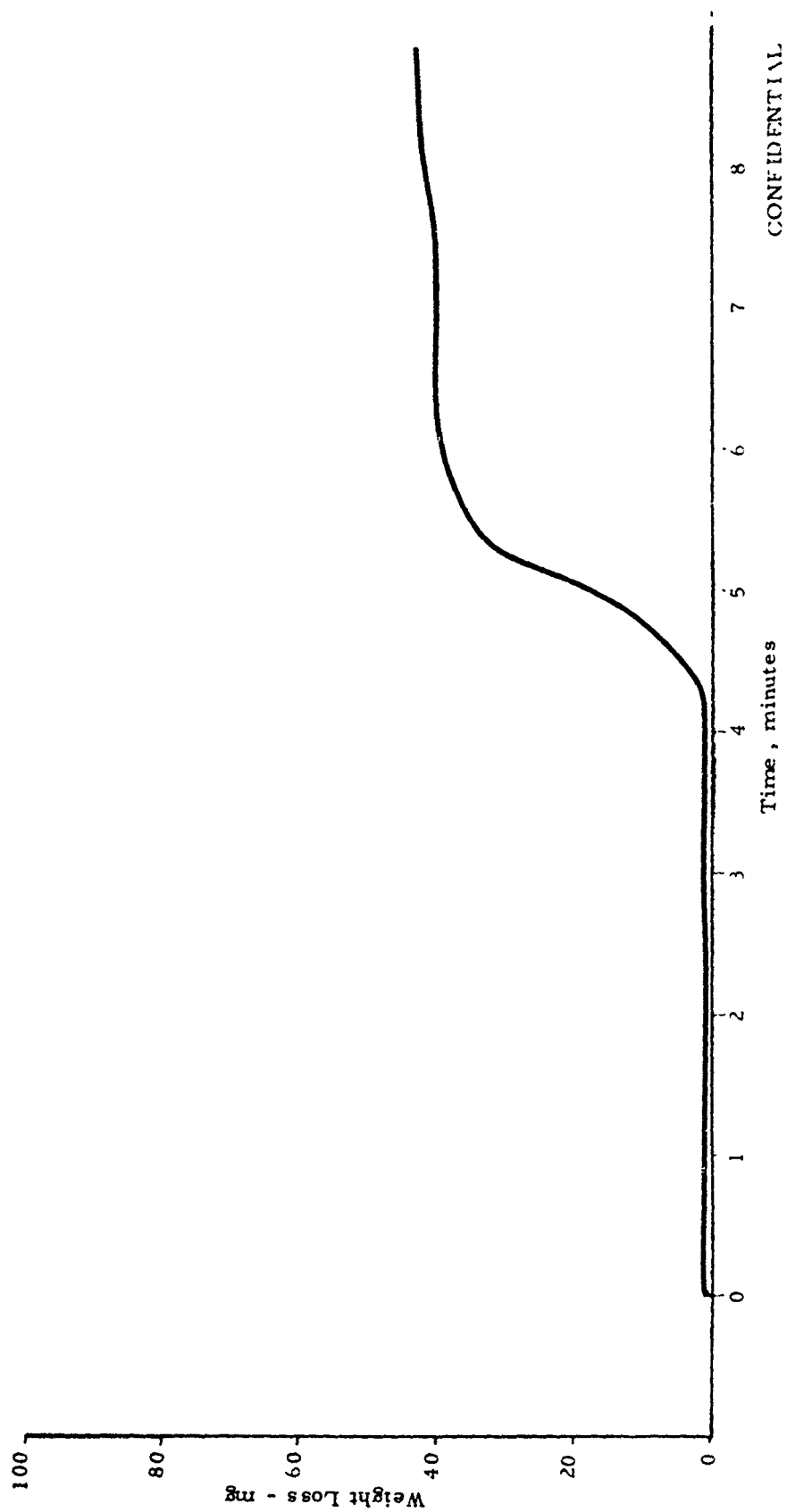
Figure 12. Constant Temperature TGA (400 mg AP - 340°C)
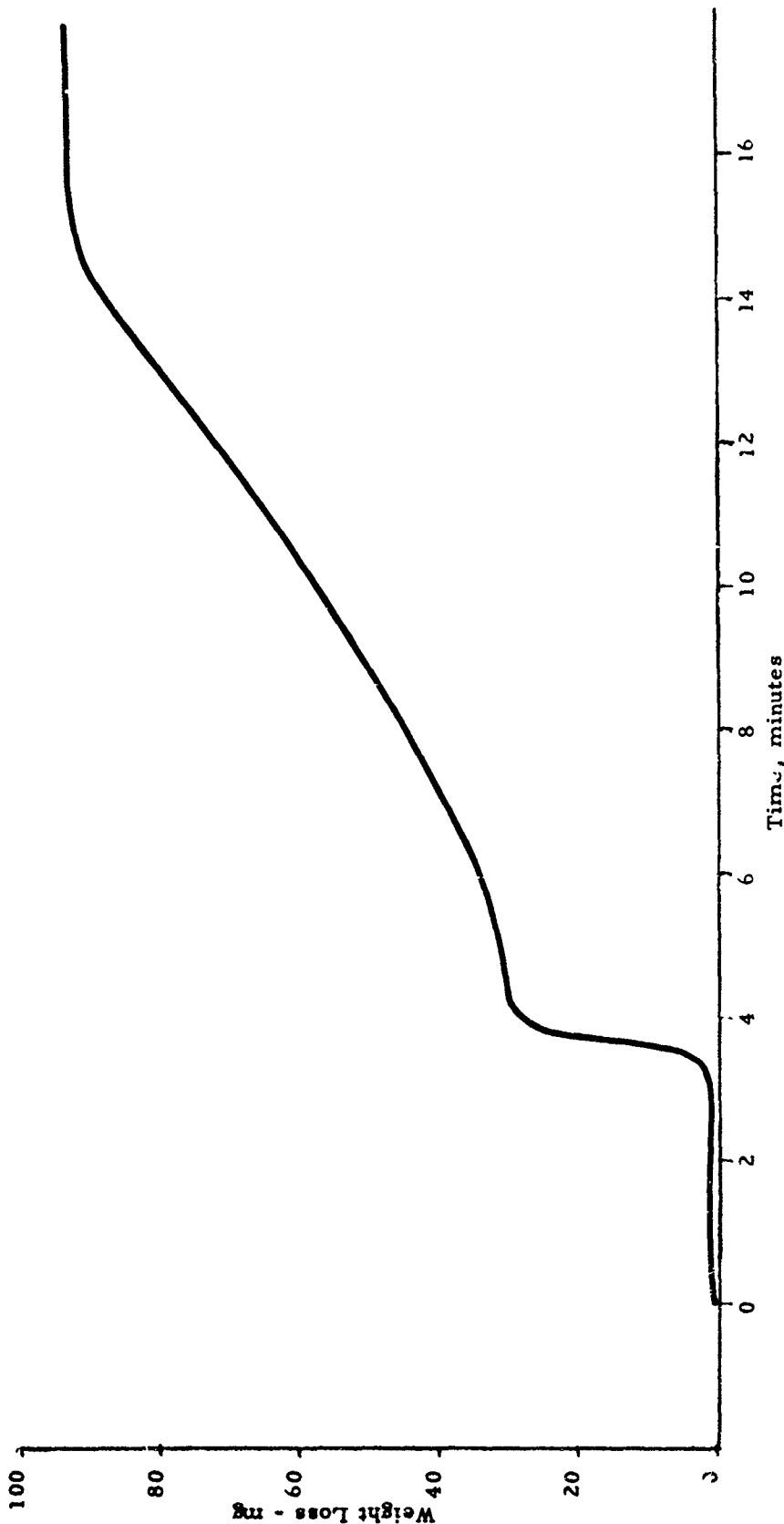
Figure 13. Constant Temperature TGA (300 mg AP - 380°C).

(U)   (2)   Complex Formulation Stu..ies

(U)   Recent work at Auburn University by J. E. Land (4) has taken exception
to not only the electron transfer mechanistic theory but also the previously
proposed mechanisms whereby transition metals enhance the decomposition
of ammonium perchlorate. This work involved DTA of mixtures of various
particle sizes of ammonium perchlorate with various concentrations of
different transition metal oxides. The basis of catalyst effectiveness was a
plot of the peak temperature of the ammonium perchlorate exotherm versus
atomic number of the metals in the catalyst. These results show that for
certain metals, from aluminum to cadmium in the periodic table, there is a
lowering of the peak temperature to a minimum at zinc. In brief, the results
show the following trend:

$$Zn > Cu > Cd > Fe > Mn > Al$$
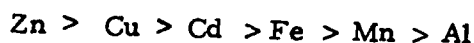
(U)   In view of these results, the very pronounced effect of zinc and cadm-
ium would seem to indicate that the ability of the metal to exist in more than
one oxidation state is not the controlling factor. Therefore, Land feels that
the proposed electron transfer is nonoperable.

(U)   The basic premise of his proposed mechanism is as follows:

(U)   The fact that ammonium perchlorate sublimes when heated is known.
In order for this to be accomplished, a proton must be transferred from the
ammonium ion to the perchlorate ion and the resultant gases vaporized. In
ionic salts a temperature of at least $480°C$ is required for the decomposition
of the perchlorate ion, and the ion itself has only a low attraction for protons.
The charge on an oxygen of this ion is calculated to be about -0.21 units. But
when a proton is accepted by the perchlorate ion, the Cl-O bond weakens and
the formed perchloric acid will decompose at $92°C$. It is therefore logical to
assume that decomposition at low temperature must initiate with perchloric
acid. However, for such an action to continue, there must be energy avail-
able to maintain burning, and Land proposes that at this point the absence of
ammonia be   nes important. The free OH radical from the decomposing
$HClO_4$ extracts hydrogen from ammonia to form water, ultimately leaving
two nitrogens to dimerize to molecular nitrogen. Something must prevent the
collision of the ammonia and the perchloric acid long enough to let the acid
start to split out OH radicals. Assume that in this brief period the ammonia
has found it possible to make a nucleophillic attack on a more desirable site
than a proton; then the $HClO_4$ would not be able to give up the proton, but
rather would exist long enough to start decomposing. Land feels that the
metal part of the catalyst traps the ammonia in the form of an ammine ligand
complex.

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(U)   Close examination of such a mechanism reveals some questions that need to be answered. First of all, the stability of a metal ammine complex at the surface temperature of decomposing ammonium perchlorate is somewhat questionable. The formation of iron ammines, in particular, is most difficult at ambient conditions and the lability of the complex should increase with increasing temperatures. Realization of this fact, in the case of iron, has led Land to further postulate that the iron may be a good complexing agent for the chlorate radical. This view has been prompted by the fact that under some non-aqueous conditions, certain metals can form rather stable complexes with the chlorate ion as the ligand.

(U)   Secondly, although the results of the DTA work indicate that zinc and cadmium would be good decomposition catalysts, the success of such compounds in helping to achieve increased burning rates in composite propellants has been somewhat less than spectacular.

(U)   The experiments conducted under the ammonia complex formation area of Thiokol's program were designed to ascertain the validity of the theory that ammonia is removed from the atmosphere of the decomposing ammonium perchlorate, thus allowing more favorable circumstances for decomposition of perchloric acid. Particularly, they were designed to determine if complexes between iron and ammonia could be formed and remain stable at temperatures corresponding to the surface temperature of a burning propellant, thus removing ammonia from the atmosphere and affecting the kinetics of the decomposition of ammonium perchlorate.

(C)   An apparatus consisting primarily of an ammonia generator, glass reaction chamber, material addition device, sample holder, temperature recorder, and heat generator was assembled. A mixture of air and ammonia gas was passed over beds of Fe_2O_3, ferrocene, and butyl ferrocene which were maintained at 350 to 360°C. The residues from these three reactions were examined by X-ray diffraction. The iron (III) oxide had been reduced to Fe_3O_4 by the hot ammonia gas. The residues from the ferrocene and butyl ferrocene experiments were amorphous. The latter residues were heated to 600°C for 2 hours in a muffle furnace, producing iron (III) oxide.

(C)   The residues from the ferrocene and butyl ferrocene decomposition were almost negligible and it is thought that the small amount of iron compound present could not be detected in the presence of the amorphous residue.

(C)   The experiment conducted with the ferrocene and butyl ferrocene was repeated. A modification in the apparatus used to conduct the experiment allowed large residues to be obtained. X-ray diffraction analyses of the residues indicated the iron from both compounds had been oxidized to Fe_3O_4.

(U)   The exact mechanism of this reaction is unclear. In the case of Fe_2O_3, it is felt that simple reduction takes place. In the case of ferrocene and butyl ferrocene, however, one does not know whether the oxygen contained in the ammonia stream initially oxidized the material to Fe_2O_3 and then this compound is reduced to Fe_3O_4 in the presence of ammonia, or whether the ferrocene materials are simply oxidized to the magnetite.

(C)   The implication of these experimental results upon the catalysis mechanism is twofold. First of all, there is not sufficient iron compound in a conventional propellant to react with enough ammonia in this redox process to significantly change the gas phase equilibrium. Secondly, the formation of Fe_3O_4 provides for facilitation of electron transfer reactions, if they do occur, because of the presence of more than one valence state of iron. However, the gaseous atmosphere surrounding a catalyst particle is, in actuality, slightly oxidizing in nature and the formation of Fe_3O_4 in the propellant combustion process seems unlikely.

(U)   If iron compounds have the same catalytic effect upon the decomposition of ammonium nitrate as they exhibit in the case of ammonium perchlorate, then there exists the possibility that some interaction between the iron compounds and ammonia is important. This would tend to support the ammonia trapping theory.

(C)   A series of DTA tests, with different oxidizers, were designed to elucidate what moiety in the decomposition of the subject materials is affected by iron containing materials. It had previously been concluded that the efficacy of iron compounds on the burning rate of ammonium perchlorate containing propellant could be attributed to the more rapid gas phase reactions; in particular, the decomposition of perchloric acid or ammonia. In order to determine which of these compounds is affected by iron compounds, samples of ammonium nitrate and potassium perchlorate were examined and comparisons made with data pertaining to ammonium perchlorate.

(U)   Differential thermal analysis tests were conducted with ammonium perchlorate, ammonium perchlorate plus iron oxide, ammonium perchlorate plus ferrocene, ammonium perchlorate plus butyl ferrocene, ammonium nitrate, ammonium nitrate plus iron oxide, ammonium nitrate plus ferrocene, ammonium nitrate plus butyl ferrocene, potassium perchlorate, potassium perchlorate plus iron oxide, potassium perchlorate plus ferrocene, and potassium perchlorate plus butyl ferrocene. The resulting data are shown on Figures 8, 10, 14 and 15.
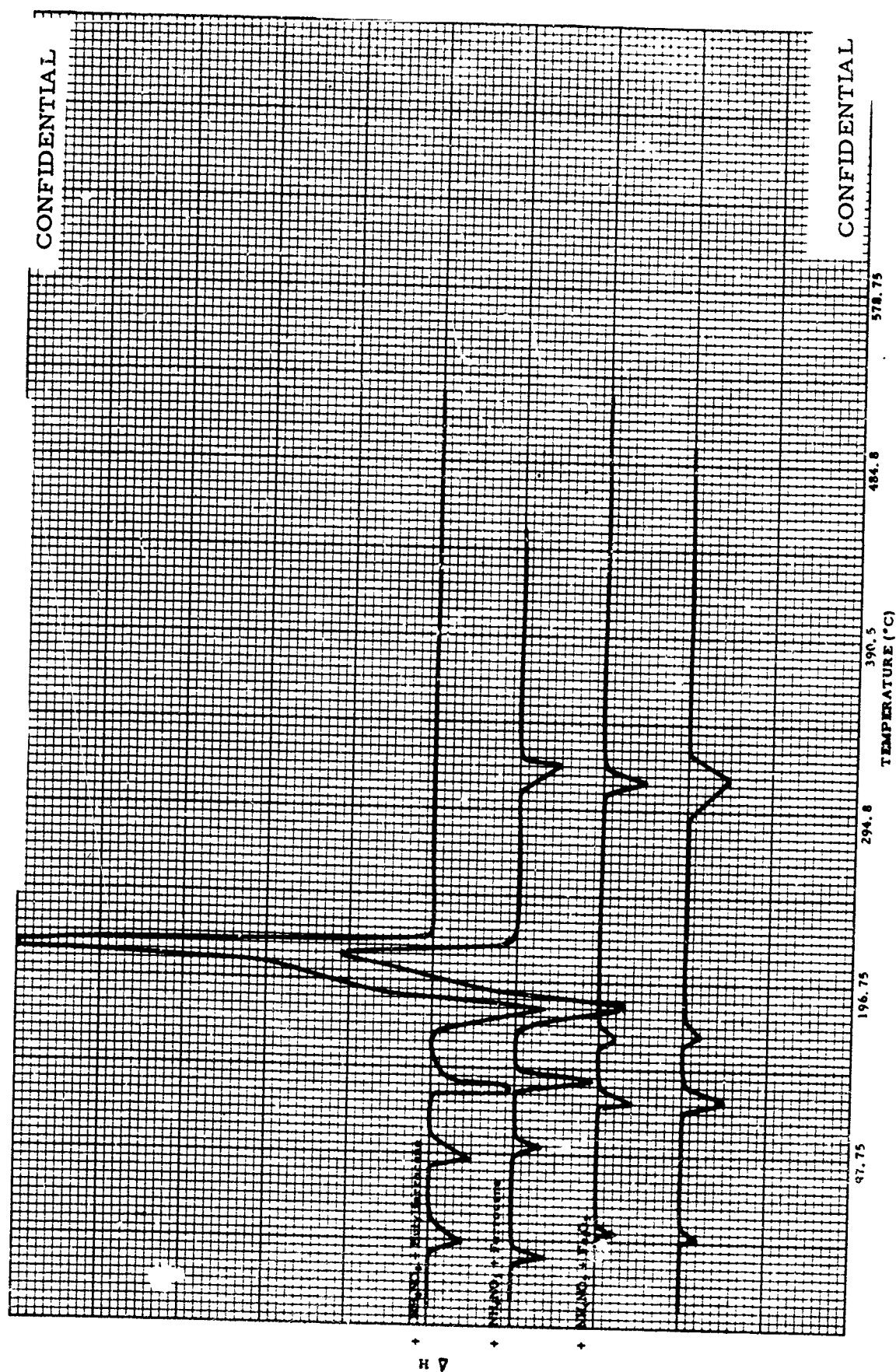
Figure 14. Differential Thermogram of NH_4NO_3 and Catalysts.

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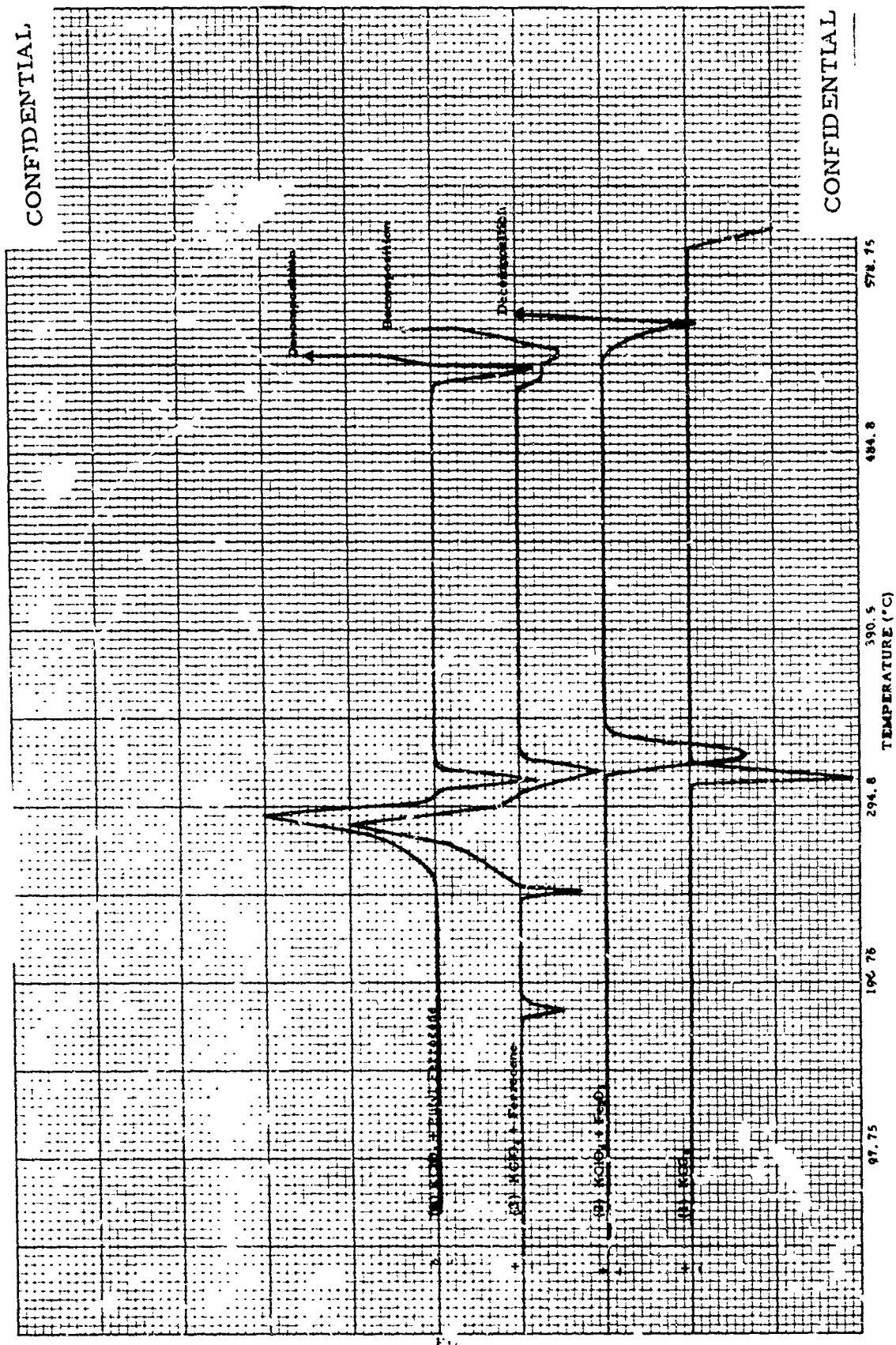
Figure 15. Differential Thermogram of KClO$_4$ and Catalysts.

(C)   It is known that one of the primary steps in the decomposition of ammonium perchlorate and ammonium nitrate is an irreversible gasification to ammonia and the respective acids. It is also known that iron oxide is not a particularly good decomposition catalyst for nitric acid. Therefore, if similar effects are noted in the thermal decomposition of ammonium perchlorate and ammonium nitrate in the presence of iron (III) oxide, it is quite clear that the interaction between ammonia and iron compounds is the one of greatest significance. However, the effect of iron (III) oxide on the decomposition of ammonium nitrate was negligible. Therefore, it appears probable that the perchloric acid is the moiety affected by the iron oxide.

(C)   It is important to point out that the exotherms noted in the case of mixtures of either ferrocene or butyl ferrocene with either oxidizer (ammonium nitrate or potassium perchlorate) can be attributed to the oxidation of the organic matter contained in the iron compounds by some preliminary decomposition products of the oxidizers.

(C)   The decomposition of potassium perchlorate is not clear cut. It is known that decomposition accompanies melting at about 580 to 590°C. However, some of the decomposition products are soluble in the molten oxidizer and interaction of these materials with potassium perchlorate cloud the kinetics of the rate determining step. It is know that perchloric acid is not one of the prime decomposition products from potassium perchlorate. Therefore, iron (III) oxide should not have a significant effect on the decomposition of potassium perchlorate if indeed the efficacy can be attributed to catalysis of perchloric acid decomposition. As the data indicates, lowering of the melting-decomposition point of potassium perchlorate was noted in the presence of iron oxide. However, the lowering is fairly insignificant percentage-wise in view of the high decomposition temperature.

(U)   (3) Perchloric Acid Decomposition Catalysis

(C)   The initial step in the decomposition of ammonium perchlorate has been shown to be the dissociation of the solid (irreversible sublimation) into perchloric acid and ammonia. A series of experiments were conducted to test the validity of the theory that the efficacy of iron (III) oxide upon the burning rate of composite propellants can be attributed to a more rapid (exothermic) decomposition of perchloric acid on the catalyst surface.

(U)   (a) Perchloric Acid (72 percent) - Catalyst Interaction

(U)   Although cold, 72 percent perchloric acid is a very poor oxidizing agent and no particular reaction would be predicted between the acid and the catalysts in question, compatibility and DTA tests were run in order to get an indication of the relative reactivities that might be encountered in our testing reactions of anhydrous perchloric acid with the respective catalysts. The results are shown below.

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	Compatibility with $HClO_4$ (72%)	DTA with $HClO_4$ (72°)
	(24 hours @ 25°C)	
Fe_2O_3	No reaction	Endotherm at 197°C (bp of $HClO_4$)
Ferrocene	Slight oxidation (appearance of the blue colored ferricinium ion)	Endotherm 90°C (ferrocene sublimation) Exotherm 217°C
Butyl Ferrocene	Slight oxidation (appearance of the blue colored ferricinium ion)	Minor Exotherm 114.5°C Major Exotherm (Explosion) 117°C

As would be expected, the results indicate that the catalysts containing organic matters reacts violently at higher temperatures with 72 percent perchloric acid, while indicating reasonable passivity at room temperature.

(U)   (b)   Preparation of Anhydrous Perchloric Acid

(U)   A 50 milliliter sample of 70 percent perchloric acid was placed in a reaction flask which was immersed in dry ice (-109°F) for cooling. Oleum (30 percent fuming sulfuric acid) in a ratio of 2.5 volume to 1 volume of perchloric acid was slowly added. The reaction flask was then mounted with the receiver, condensing column, acid fume and moisture eradicators, and other associated equipment. Extreme care was taken to remove all contaminants from the apparatus prior to assembly. The ball-joints of all glassware were sealed with 70 percent perchloric acid. Dry ice provided cooling for the reaction flask and the moisture trap. The experimental apparatus is depicted on Figure 16.

(C)   The reaction was started by reducing the internal pressure to 0.8 millimeters with the reaction mixture initially at dry ice temperature. The temperature was allowed to slowly rise to 25°C during the distillation. A vigorous volatilization occurred initially, subsiding to a slow bubbling of gaseous perchloric acid that broke the surface to the reaction mixture as though it were a boiling phenomenon. After the reaction had gone to completion, internal pressure was allowed to slowly return to atmospheric pressure.

1. Thermometer
2. Distillation Flask
3. Dry Ice
4. Receiving Flask
5. Condensation Column
6. Acid Scrubber (With KOH Pellets)
7. Condensation Tube
8. T Joint
9. Tube of Dryrite
10. H_2O Inlet
11. H_2O Outlet
12. To Stoke's Gage
13. To Vacuum
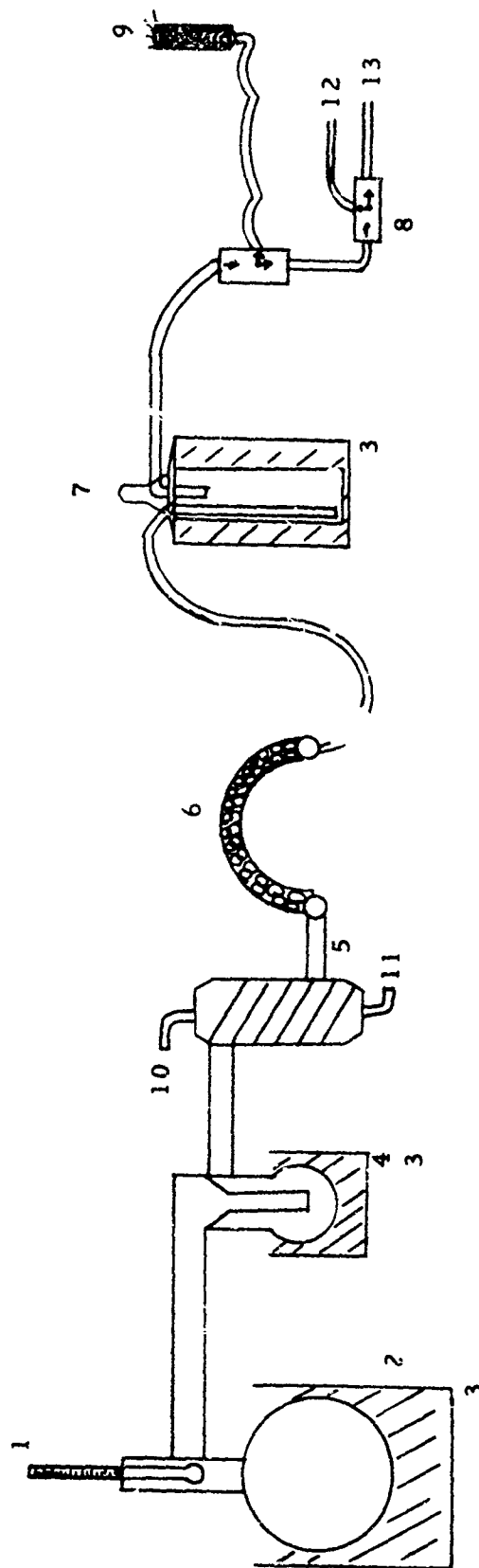
Figure 16. Anhydrous Perchloric Acid Distillation Apparatus.

The receiving flask was removed and immediately sealed while being retained in dry ice. A yield of 10 to 15 percent of theoretical was obtained.

(U)   (c) <u>Anhydrous Perchloric Acid Decomposition</u>

(U)   If, as had been postulated, the efficacy of iron compounds in increasing the burning rate of composite propellants can be attributed to more efficient decomposition of perchloric acid on the surface of iron oxide, then a measure of the relative decomposition rates of the acid, both pure and in the presence of iron (III) oxide, was in order.

(U).   Small acid-analysis thin-walled glass bulbs with extended capillary tubes were prepared. The capillaries were then inserted into the acid through a small hole made in the glass top which shielded the anhydrous perchloric acid from the atmosphere. Heat was applied to the receptacles, thus causing acid to flow into the bulbs upon cooling. After 2 milliliters of acid had flowed into the receptacles, they were removed and sealed by passing the capillary arms through a flame.

(U)   Samples of iron oxide, ferrocene, and butyl ferrocene were inserted and sealed in glass bulbs very similar to the acid-analysis containers. One sample of anhydrous perchloric acid, catalyst, and a glass rod (used as a striker to fracture the glass bulbs) were then inserted into a 100-milliliter test tube and sealed with a flame. Test tubes were also prepared which contained no catalysts so that the reaction rate of perchloric acid with temperature could be determined. The anhydrous perchloric acid was maintained essentially at dry ice conditions throughout the above-mentioned preparations.

(U)   A constant temperature (60°C) water bath was prepared. A safety shield was inserted in front of the apparatus. An operator stood behind the shield, and, with the aid of long tongs, ruptured the glass bulbs containing the materials to be studied by vigorously agitating the test tube, and immediately dropping the reactants into the water bath. A metal weight attached to the test tube submerged it.

(C)   The reaction time recorded was the time required to fracture the test tube by internal pressure. The average time required for anhydrous perchloric alone was 55 minutes; the reaction time of the acid and iron oxide was 2 to 4 minutes. The reaction time for either ferrocene or butyl ferrocene and the acid was not accurately determined since instantaneous explosions occurred.

(C)   The same general apparatus as used above to prepare anhydrous perchloric acid was again utilized with only minor modifications to the apparatus and technique. A yield of 20 to 25 milliliters of anhydrous perchloric acid (approximately 60 percent of theoretical) was obtained.

(U)   The reaction time of perchlorate acid alone and in the presence of various other materials was then determined. Reaction time was measured as the time required to rupture sealed glass sample bottles at $67°C^3$. The materials studies were inert and presented only different type and size surface areas for the thermal decomposition of the anhydrous perchloric acid. The materials studied, along with the associated retention times, are listed below:

Material	Reaction Time
$HClO_4$	60 minutes
$HClO_4$ + 400μ ground glass	60 minutes
$HClO_4$ + 36 μ ground glass	8 seconds
$HClO_4$ + Fe_2O_3 (0.1 - 1.0μ)	5 seconds
$HClO_4$ + Fe_3O_4 (0.2 - 1.0μ)	5.5 seconds
$HClO_4$ + Crystalline Al_2O_3 (Alundum)[4] (180μ)	6 seconds
$HClO_4$ + CuO (0.2 - 2.0μ)	6 seconds

(C)   Care was taken to insure complete dryness of the catalytic surface but no attempt was made to purify the materials. For instance, the Alundum may have contained traces of aluminum, which could have initiated the very fast reaction noted. Nevertheless, this series of experiments shows that the decomposition of $HClO_4$ is dependent to a great extent upon the surface area of inert material upon which decomposition could possibly take place. The decomposition seems to be somewhat independent of the chemical nature of the catalytic materials, with the exception of Alundum, and the purity of the Alundum puts that data point in question.

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3. The tubes to be ruptured in this set of experiments were extremely thin walled and therefore times to overpressurization were considerably shorter than those in the previous experiments.

4. Trademark for a line of fused-alumina refractory and abrasive products supplied by Norton Company, Worcester, Massachusetts.

(U)　　　　　　(d) High Pressure Studies

(U)　　In order to more closely simulate actual propellant deflagration conditions, a DTA unit, capable of operation at pressures as high as 2,000 psi, was utilized for oxidizer, binder, and catalyst decomposition studies. A schematic of the furnace and pressure assembly is shown on Figure 17. The pressure unit for the DTA apparatus was installed and calibrated. A series of experiments, completing Phases I and II high pressure studies, was run and the results are discussed in the following sections.

(U)　　　　　　(1) Ammonium Perchlorate

(U)　　A DTA of pure ammonium perchlorate was run at 200 psig (Figure 18) The effect of pressure upon decomposition is to cause oxidizer decomposition to occur at one point (350 to 380°C). This is quite important in determining the kinetics of oxidizer decomposition under burning propellant conditions since the activation energy appears to be constant and all decomposition occurs through the same mechanism. The mechanism of the decomposition under pressure has not been defined but one would expect a proton transfer reaction to be rate determining:

$$NH_4^+ + ClO_4^- \rightarrow "NH_3 \cdot HClO_4" \rightarrow NH_3 + HClO_4$$
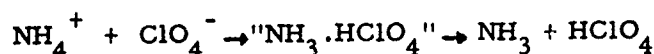
(U)　　　　　　(2) Ammonium Perchlorate and Iron Oxide

(C)　　A 1/1 mixture by volume of ammonium perchlorate and iron (III) oxide, run at 200 psig (Figure 19), revealed a single, one-phase decomposition at 305°C, approximately 50 degrees lower than the decomposition of pure ammonium perchlorate. As the iron oxide content increases, the temperature of oxidizer decomposition is lowered. The quantitative effect determined by varying iron oxide concentration and measuring temperatures of decomposition is reported elsewhere in this report.

(U)　　　　　　(3) Ammonium Perchlorate and Ferrocene

(C)　　A 1/1 mixture by volume of ammonium perchlorate and ferrocene, run at 200 psig, exhibited an endotherm at 178°C, due to the melting of ferrocene, followed by a slight exotherm, due to partial oxidation of ferrocene (Figure 20). The decomposition of oxidizer occurred at a temperature below that of the crystalline phase change of ammonium perchlorate.

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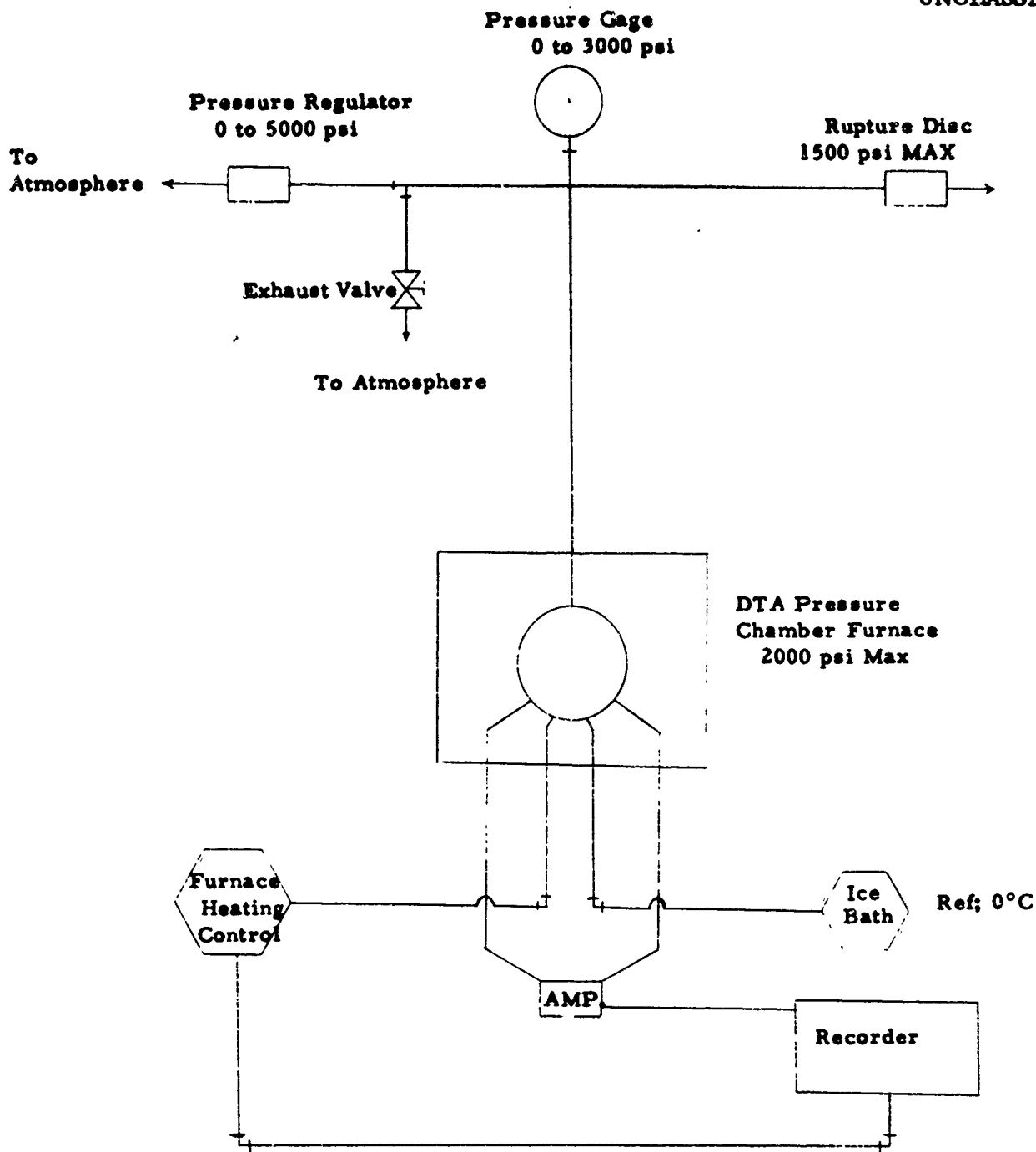
Figure 17. Schematic of Instrument Arrangement.
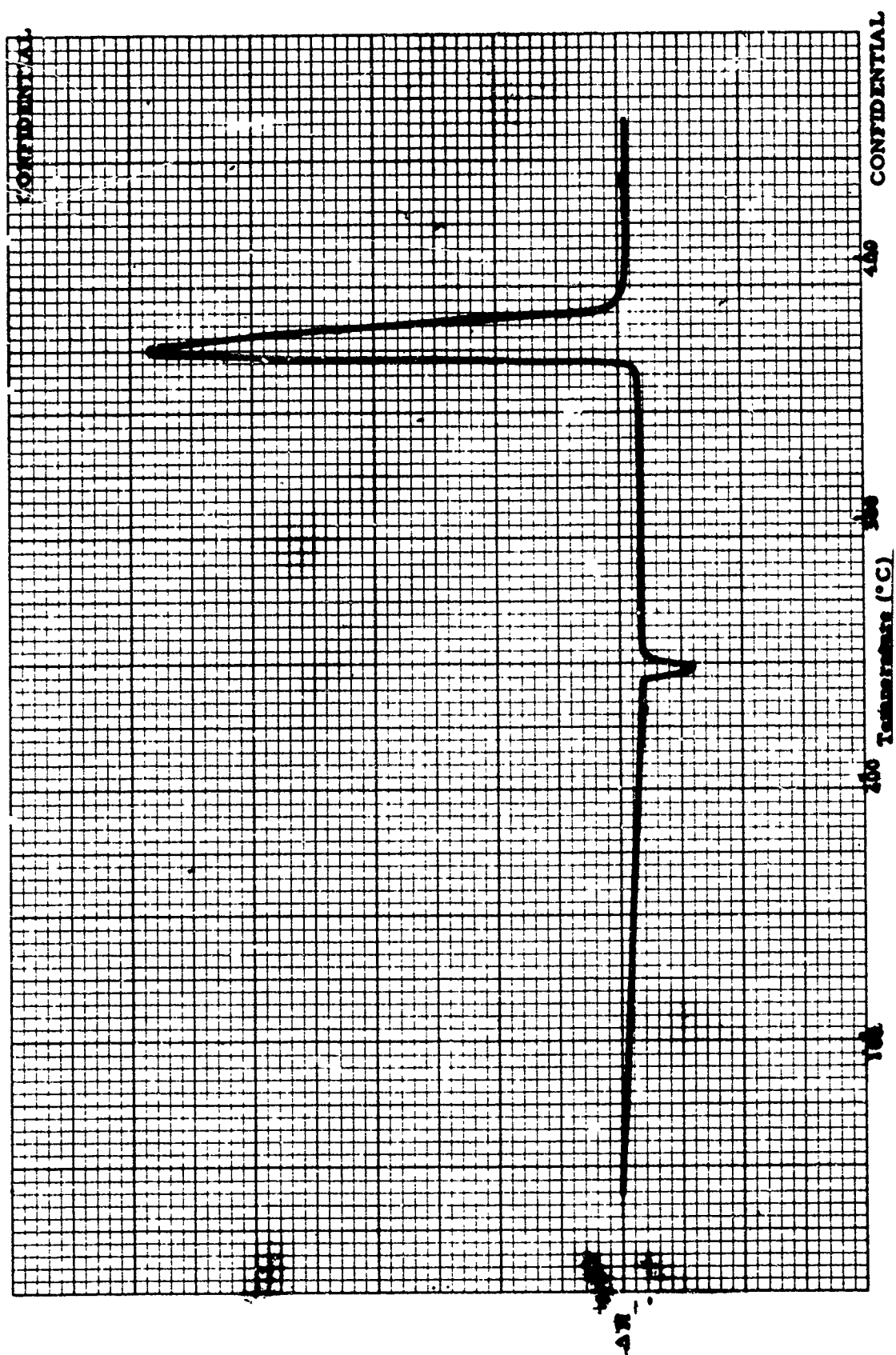
Figure 18. DTA of Ammonium Perchlorate Under 200 psig N_2.
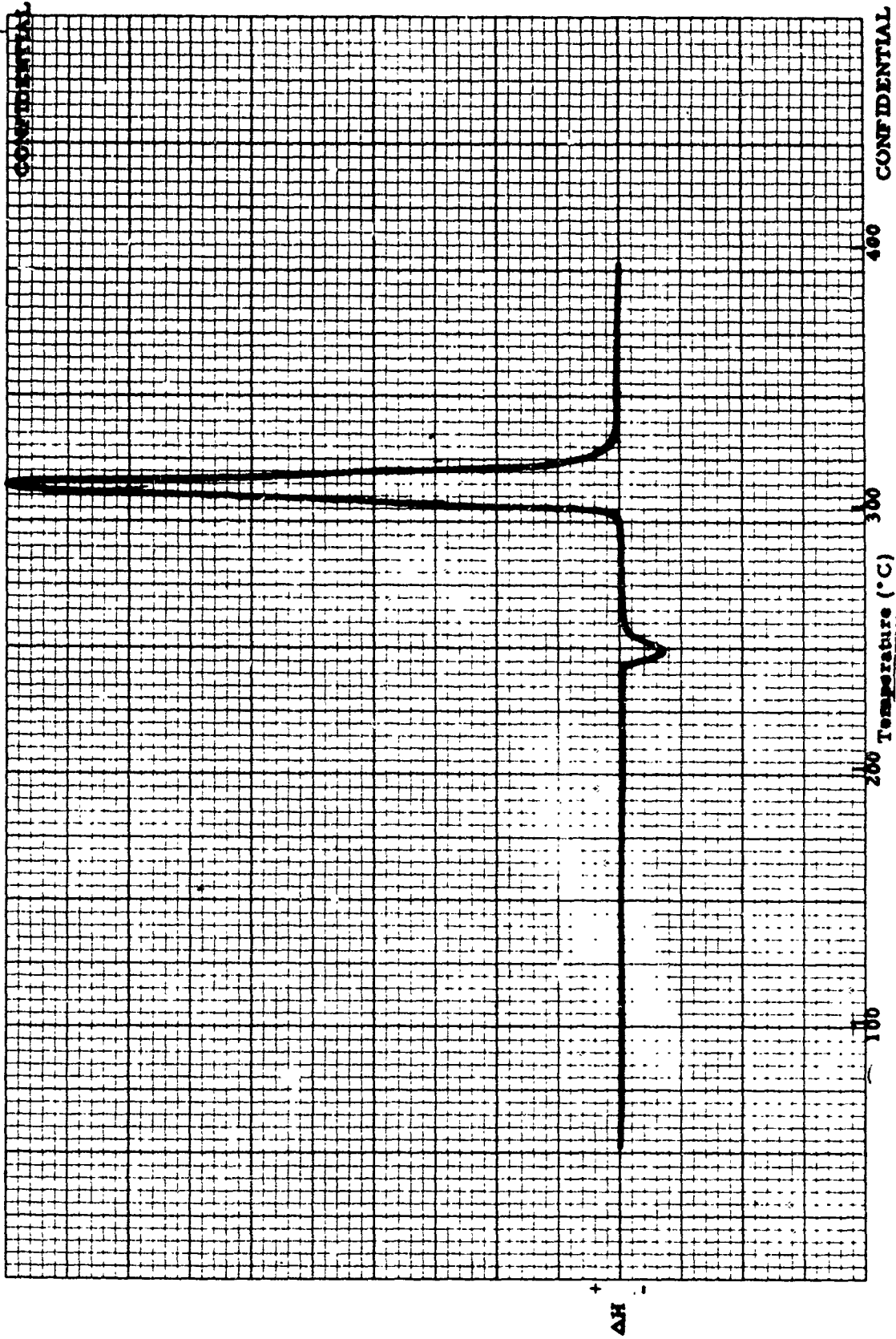
Figure 19. DTA of Ammonium Perchlorate/Iron Oxide Under 200 psig N_2.
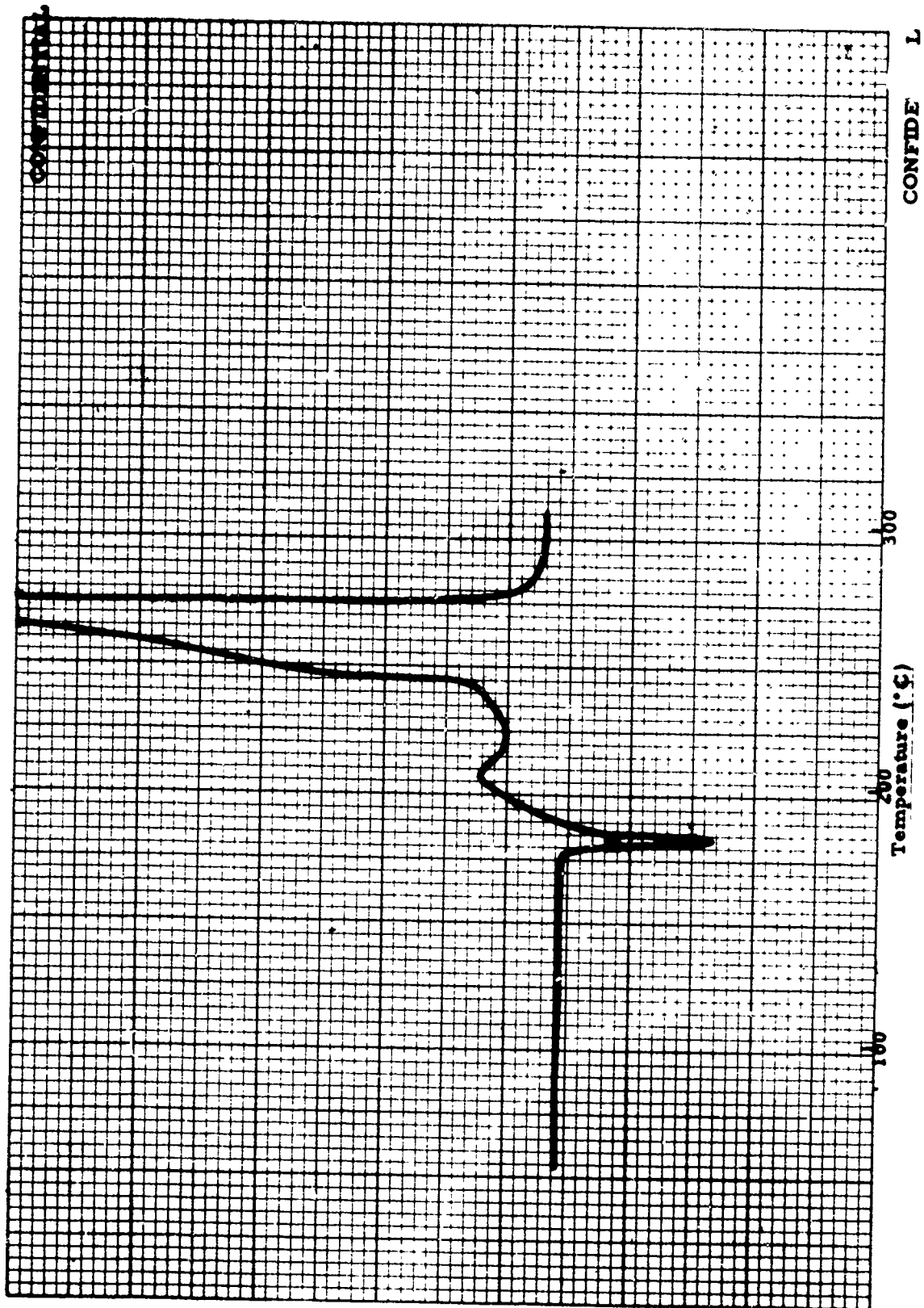
Figure 20. DTA of Ammonium Perchlorate/Ferrocene Under 200 psig N_2.

(U)   (4) Ammonium Perchlorate and Butyl Ferrocene

(C)   A DTA of a mixture of ammonium perchlorate and butyl ferrocene,
ran at 200 psig, resulted in complete decomposition of the oxidizer at 220°C
(Figure 21). Total decomposition was preceded by a relatively slow exothermic
reaction, which was initiated at 180 to 190°C.

(U)   (5) Heat Release Measurements from Ammonium
                           Perchlorate Decomposition

(C)   There has been some indication in the past that more heat was evolved
when a given weight of ammonium perchlorate was decomposed in the presence
of iron oxide than when decomposed alone. In order to obtain a semiquantitative
measure of the aforementioned thermal phenomena, a sample of ammonium
perchlorate (0.0267 grams) was decomposed in the DTA apparatus at a constant
rate of temperature rise and 200 psig (Figure 22). The area under the exo-
thermic peak, which is a reasonable measure of heat release, was measured.
This experiment was repeated several times with varying amounts of Fe_2O_3
and ammonium perchlorate. In each case more heat was released when the
oxidizer was decomposed in the presence of iron (III) oxide. The percentage
increases ranged from 25 to 42.

(U)   The ramification of these measurements must result in one of two
hypotheses:

(U)   1) The mechanism of oxidizer decomposition must be different
                 in the presence of iron oxide (different products formed) than
                 when decomposed alone.

(U)   2) The mechanism is the same in the presence of catalysts but
                 the reaction is forced further towards completion in the presence
                 of iron (III) oxide, thus resulting in greater heat release.

(C)   Although no experimental evidence is available for either postulation,
it is felt that the latter is most plausible in the light of reasoning that the
decomposition reaction is catalyzed on the surface of the iron oxide particles,
resulting in most reactive species being very close to the decomposing
oxidizer surface. These species could then react to a greater extent before
being expelled from the heated area of decomposition.

(U)   (6) Effect of Pressure on the Differential Thermal Analysis
                           of Ammonium Perchlorate/Fe_2O_3 Mixture

(C)   Samples of ammonium perchlorate (0.040 grams) were mixed with
0.0037 grams of Fe_2O_3 and the differential thermograms obtained at 100, 200
500 and 800 psig are shown on Figure 23. In general, a very slight increase

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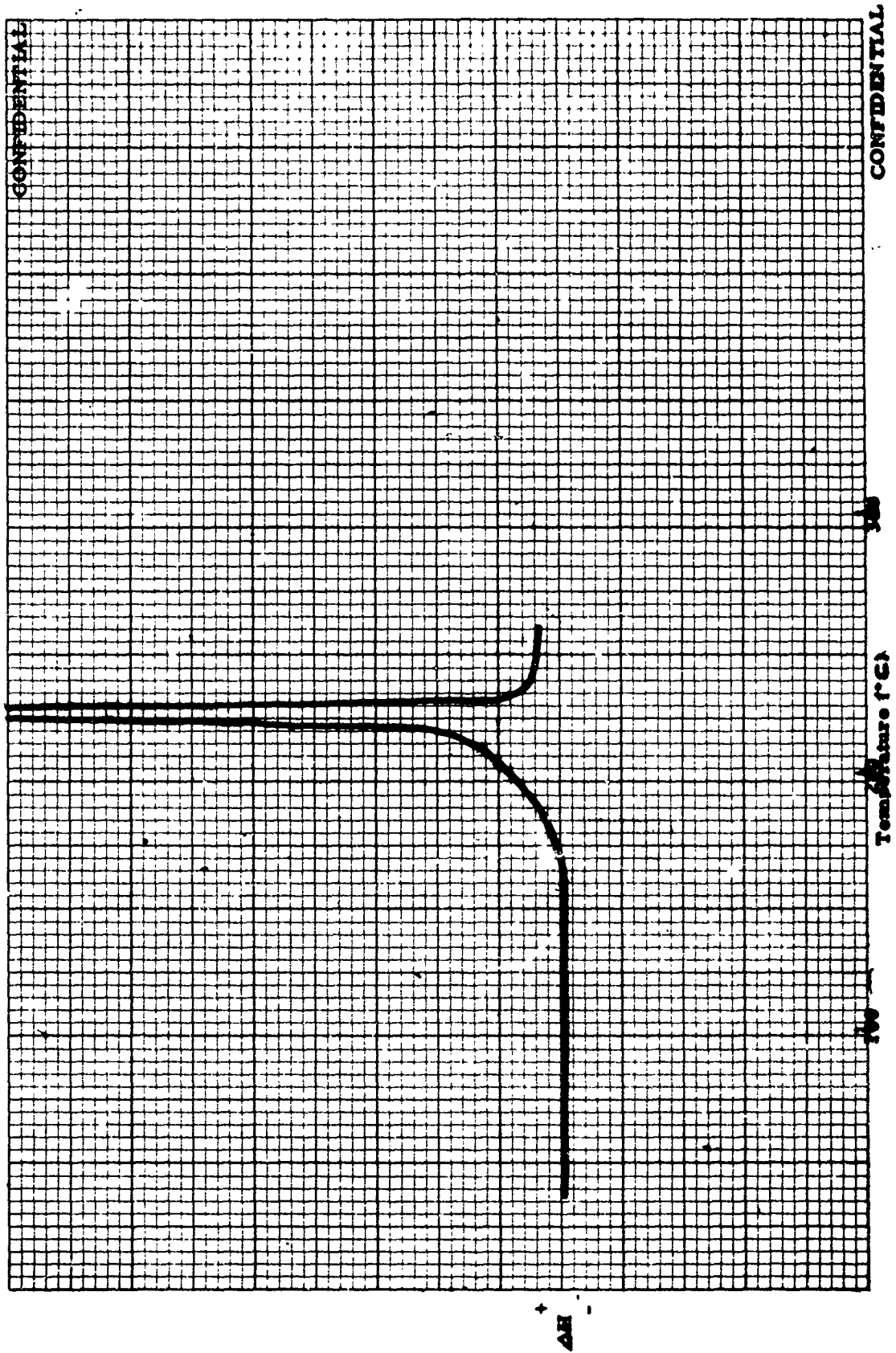
Figure 21. DTA of Ammonium Perchlorate/Butyl Ferrocene Under 200 psig N_2.
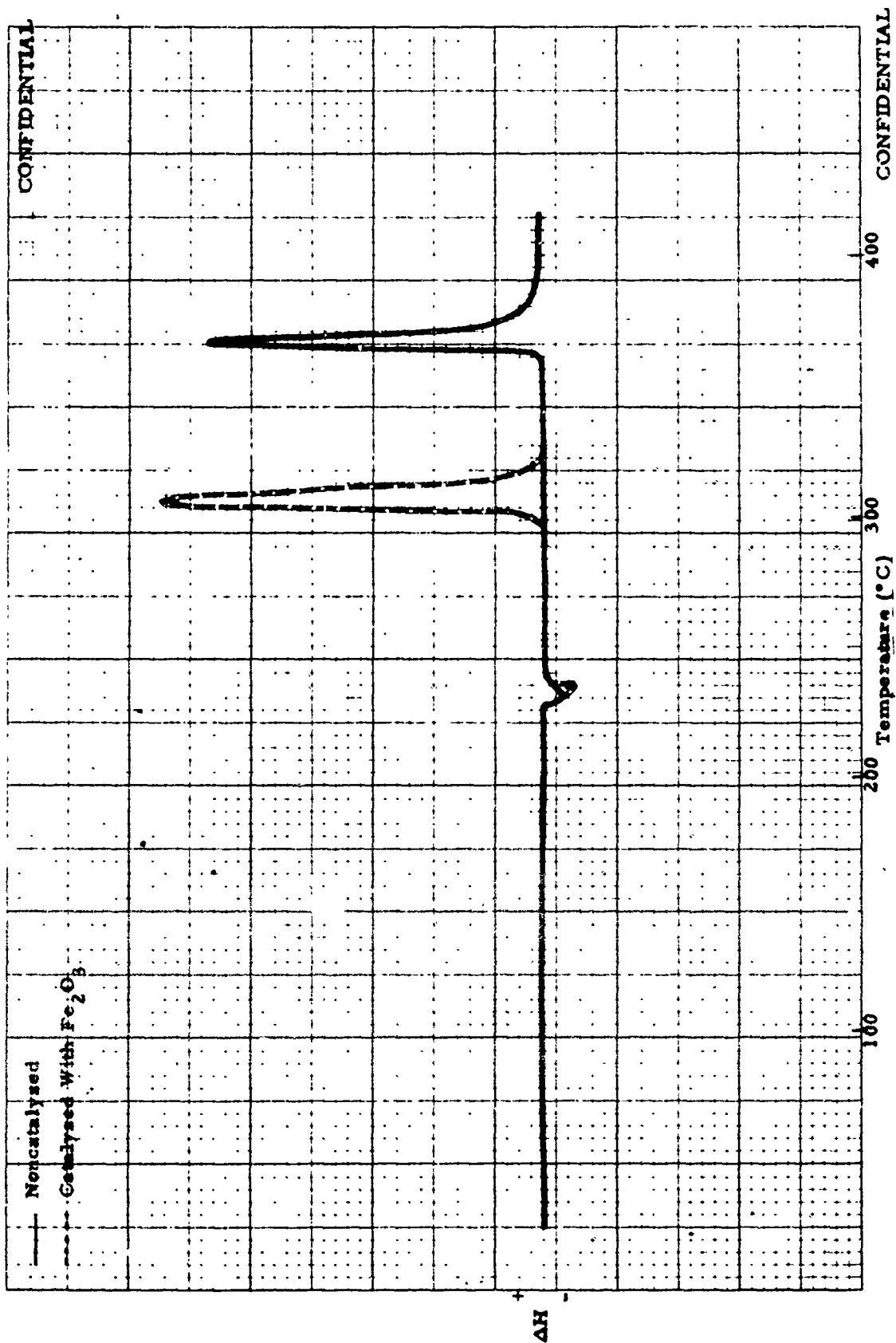
Figure 22. DTA of Ammonium Perchlorate Under 200 psig N_2.
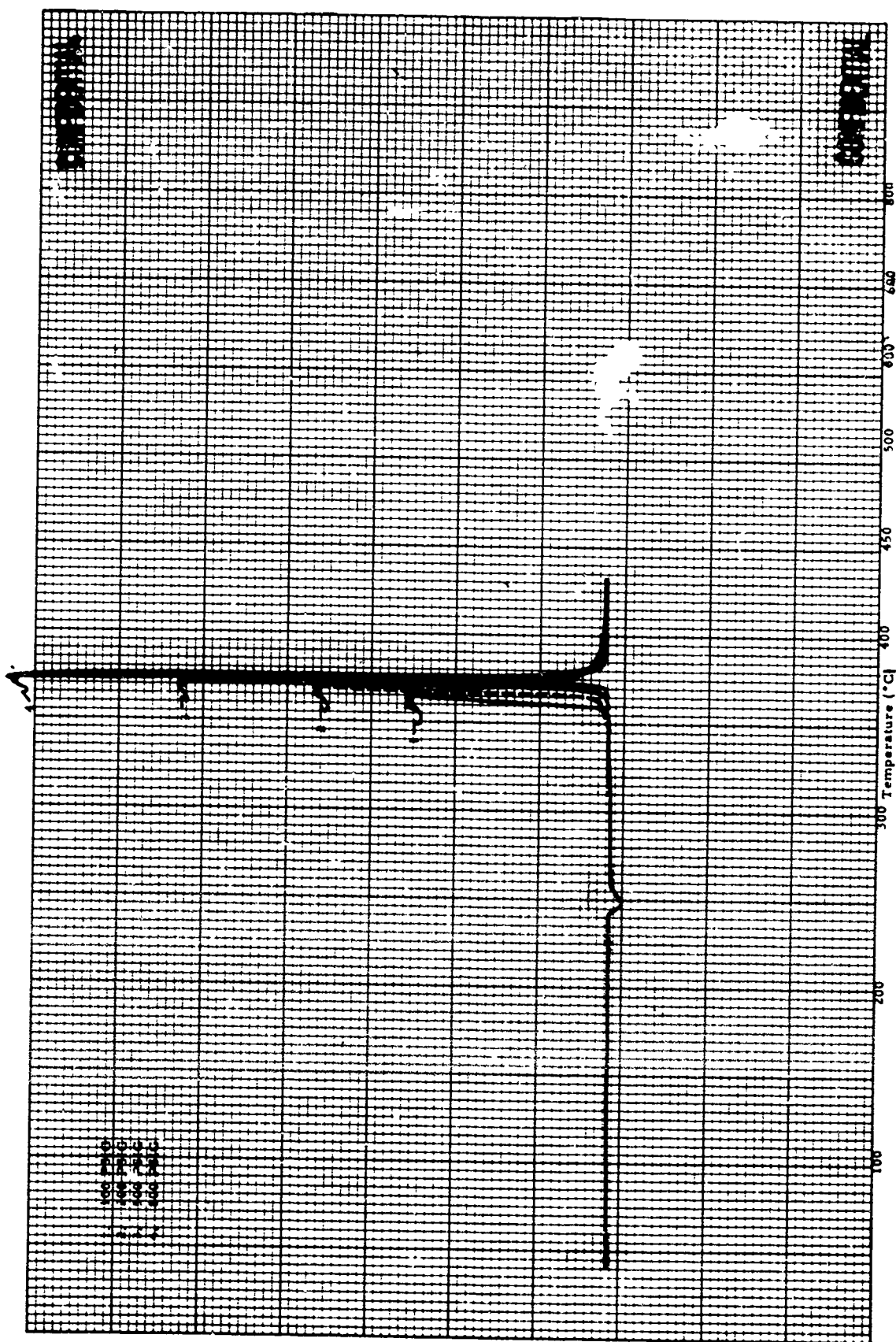
Figure 23. DTA of a Mixture of 0.04 Grams NH_4ClO_4 and 0.0037 Grams of Fe_2O_3 Conducted at 100, 200, 500, and 800 psig of N_2.

in decomposition temperature resulted from the increased pressure. However, such an observation may be within experimental error. The primary result to be noted is the increased intensity of the ammonium perchlorate decomposition exotherm with increasing pressure. This observation indicates a gas phase catalysis reaction; i.e., the oxidizer decomposition reactions are forced to occur closer to the decomposing oxidizer surface, thus resulting in greater heat feedbacks.

(U)   (7)   Effect of Varying Amounts of Fe_2O_3 upon Decomposition of Ammonium Perchlorate at 500 psig

(U)   Samples of ammonium perchlorate (0.04 gram) were mixed with varying amounts of iron (III) oxide and the resultant differential thermograms (Figure 24) indicated the following conclusions:

(C)   1) The decomposition temperature of ammonium perchlorate decreases with increasing iron (III) oxide content.

(C)   2) There is no meaningful correlation between the intensity (peak height) of the exotherm and the iron (III) oxide content.

(U)   (8)   Effect of Pressure Upon the Decomposition (Deflagration) of a Non-Catalyzed Composite Propellant

(C)   Samples of an 84 percent total solids propellant were decomposed under varying pressures in the DTA unit. The differential thermograms, plotted on Figure 25, show that the decomposition temperature decreased with increasing pressure. This was not the case with mixtures of Fe_2O_3 and ammonium perchlorate. Increasing pressure also depressed the slow rising exotherm prior to the crystalline transition point of ammonium perchlorate. This decrease in heat release with increasing pressure cannot be fully explained at this time.

(U)   (9)   Effect of Iron (III) Oxide Upon the Decomposition of Composite Propellant

(C)   An ammonium perchlorate oxidized propellant, both with and without 0.5 percent Fe_2O_3 as a burn rate catalyst, was examined by DTA (Figure 26). A reduction in decomposition (deflagration) temperature, as well as more energetic preliminary exotherms, occurred when the iron oxide was present. It is believed that the shift of the crystalline transformation endotherm to lower temperatures in the presence of Fe_2O_3 can be attributed to experimental error.

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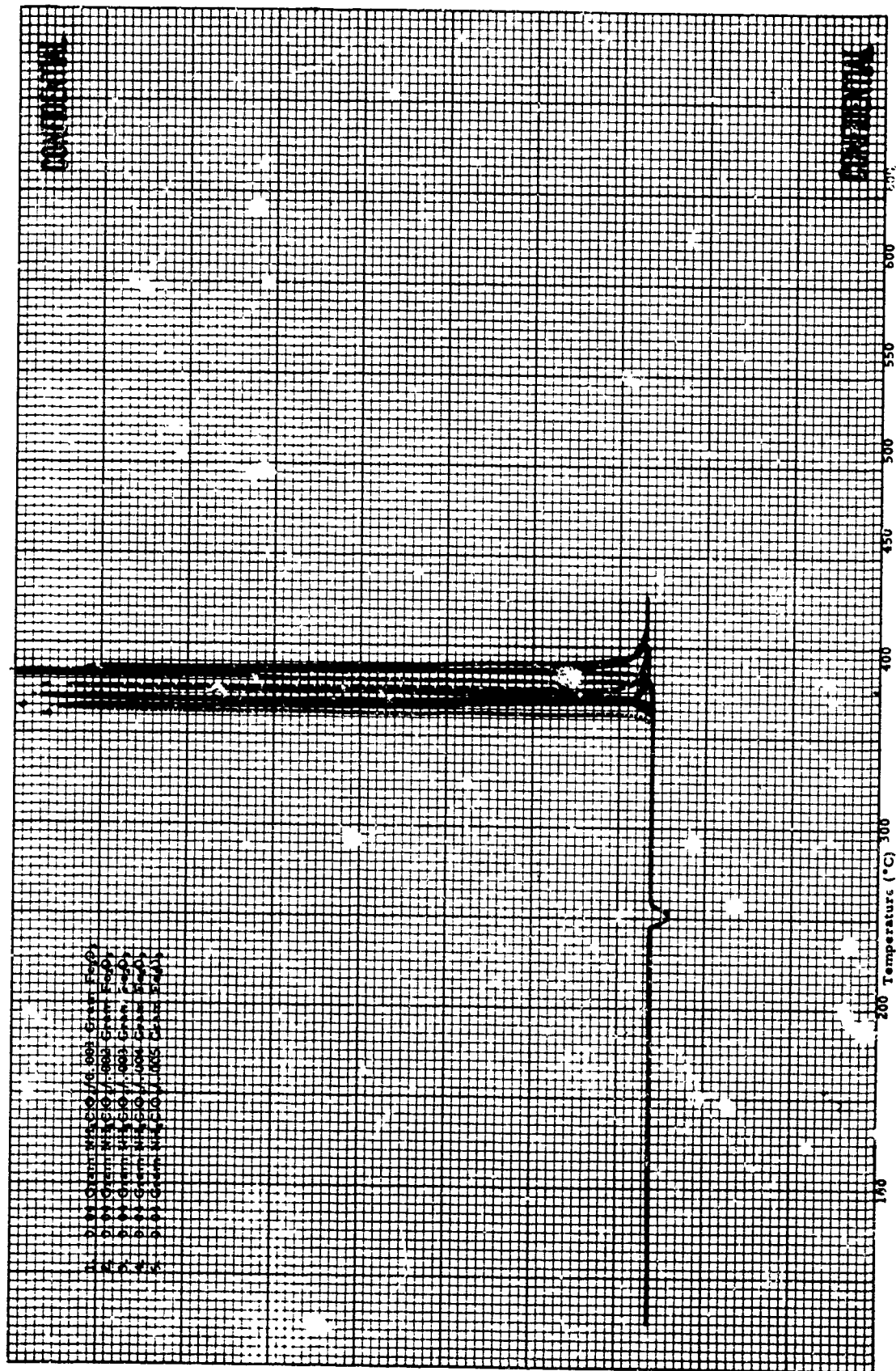
Figure 24. DTA of NH_4ClO_4 Containing Various Concentrations of Fe_2O_3 and Conducted at 500 psig of N_2.
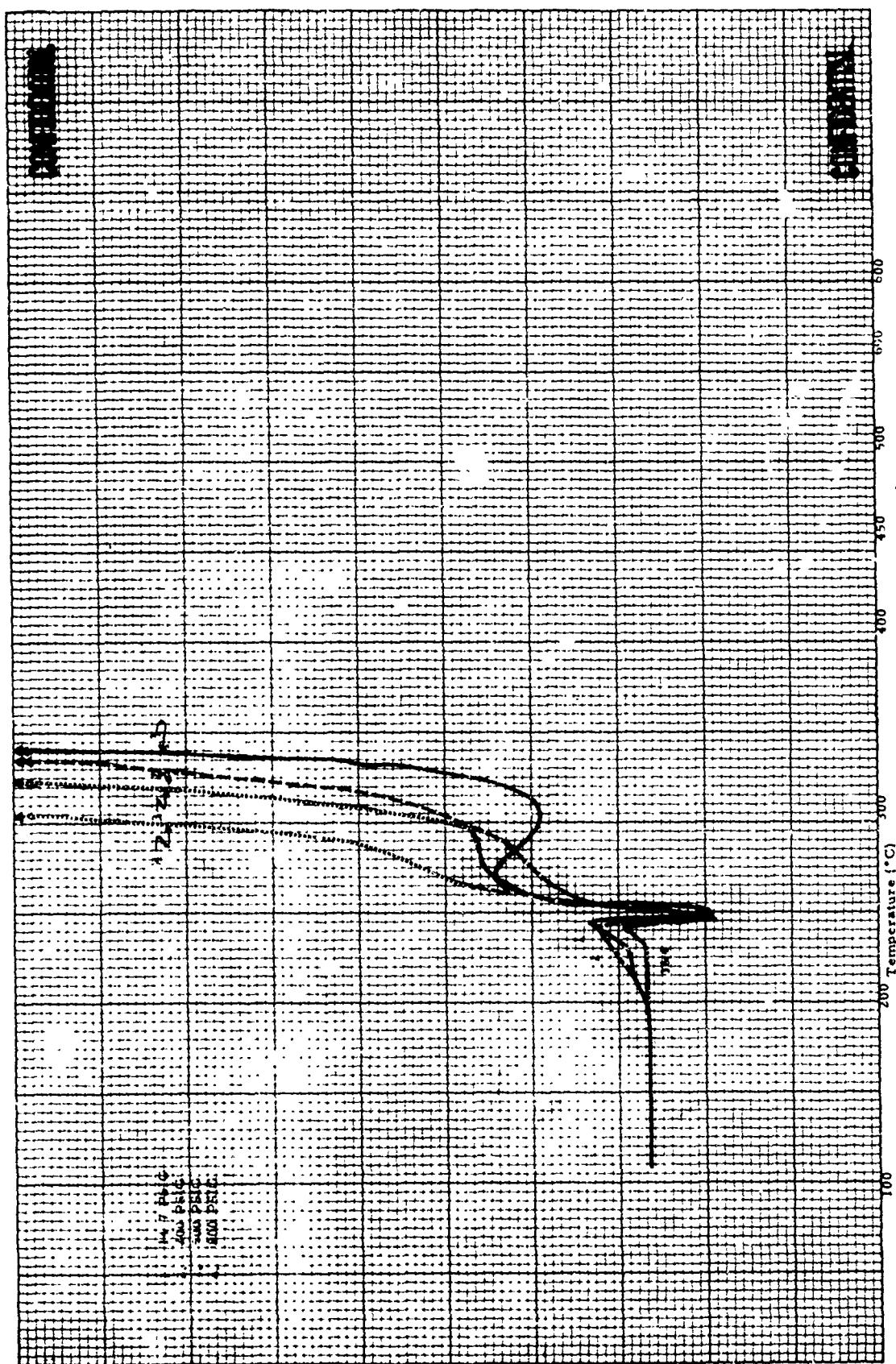
Figure 25. DTA of a Non-Catalyzed Propellant Containing 84% Total Solids at 14.7, 200, 500 and 800 psig (N_2 Atmos.).
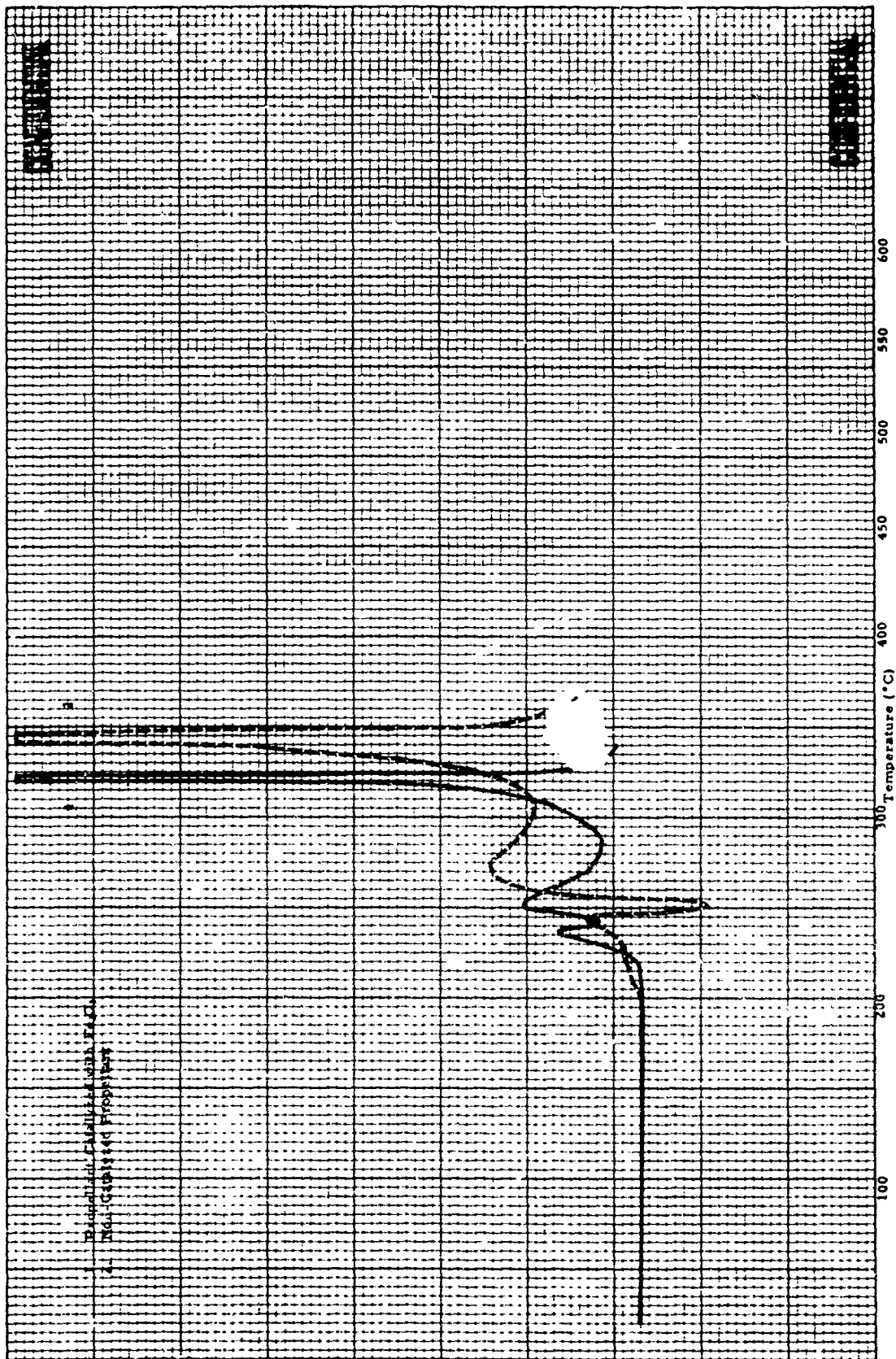
Figure 26.   DTA of an 84% Total Solids Propellant, Non-Catalyzed, versus 0.5 % Fe_2O_3, Conducted at Atmospheric Pressure.

(C)   The effect of pressure upon the DTA of the Fe_2O_3 (0.5 percent) cata-
lyzed propellant is shown on Figure 27. All phases of the decomposition are
identical with the exception of a substantial lowering of the deflagration
temperature with the increased pressure.

(U)   (10) Effect of Fe_2O_3 Specific Surface on Burning Rate

(C)   Additional experiments were conducted in order to confirm earlier
experimental results that had indicated that the higher the specific surface of
iron (III) oxide, the higher the resulting burn rate of the propellant. Two
samples of TP-H8041 propellant were prepared containing two different lots
of Fe_2O_3, which were identical with the exception of specific surface. The
propellant composition, together with the specific surface of the two lots of
Fe_2O_3 utilized, is shown below:

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Modified TP-H8041 Propellant

	Weight, %
Ammonium Perchlorate	68
Aluminum	16
PBAA	15
Fe_2O_3	1

Fe_2O_3	Specific Surface $\frac{m^2}{g}$
RY-8095	19.4
RY-2196	10.0

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(U)   The strand burn rates obtained with the two lots of Fe_2O_3 are given
below and are compared to the burn rate of the TP-H8041 propellant without
iron oxide.

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	Burning Rate at 1,000 psi (in/sec)
TP-H8041	0.37
TP-H8041 + 1% RY-2196	0.401
TP-H8041 + 1% RY-8095	0.44

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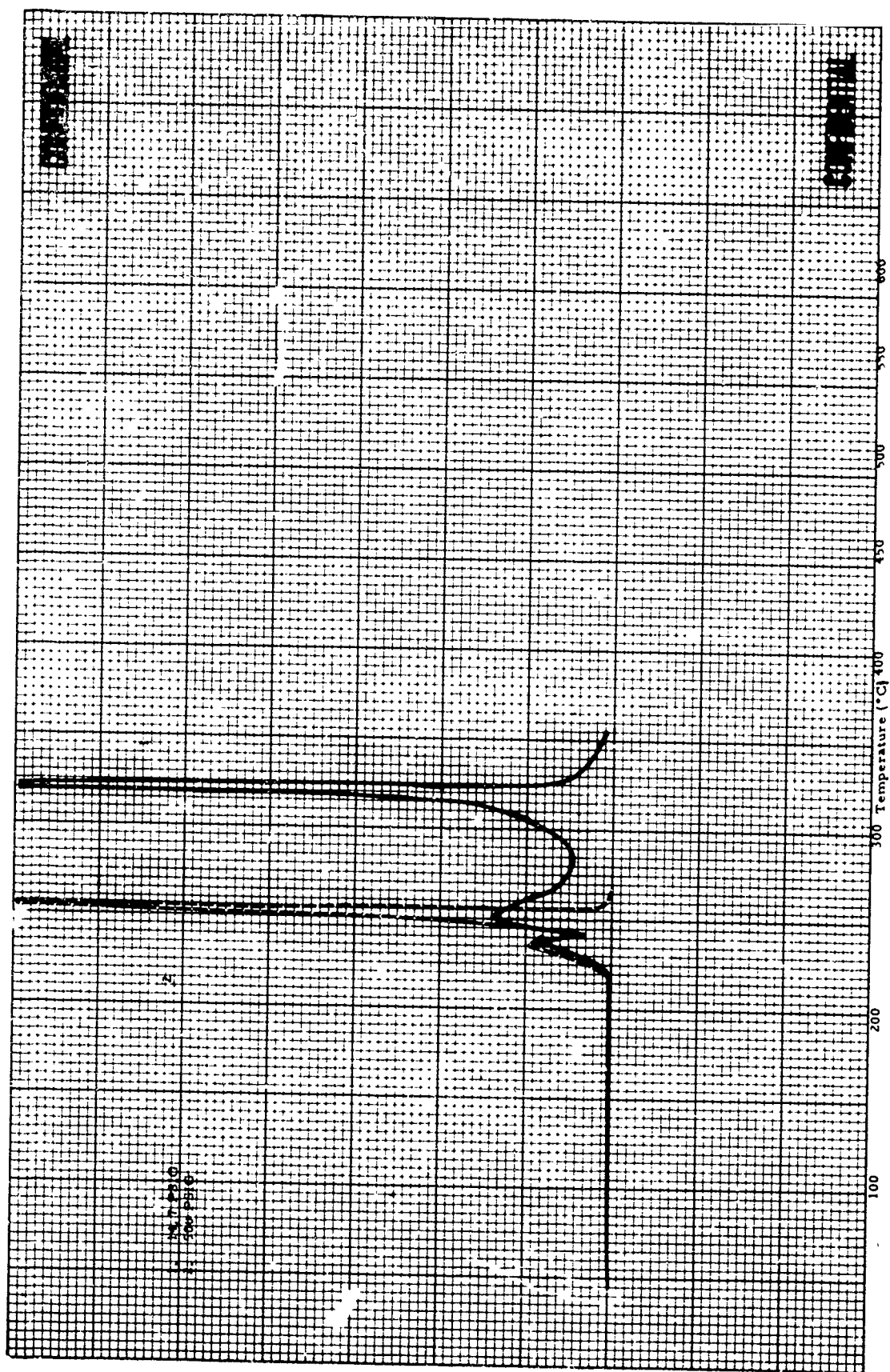
Figure 27. DTA of an 84% Total Solids Propellant Catalyzed with 0.5% Fe_2O_3, Conducted at 14.7 and 500 psig (N_2 Atmos.)

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(C)   The correlation resulting from these data is as predicted; however, as the concentration of iron (III) oxide is increased (e.g., 3 percent) the differences between lots of Fe_2O_3 are somewhat dampened simply because such a concentration provides a total specific surface which would be required for more ideal catalysis.

(U)   (11) Ease of Catalyst Oxidation upon DTA Exotherm in
                       Ammonium Perchlorate Decomposition

(C)   Three samples of ferrocene derivatives, which are less susceptible to air oxidation than are ferrocene or butyl ferrocene, were provided by Lt. C. Pittman of the U. S. Army Missile Command. These compounds are:

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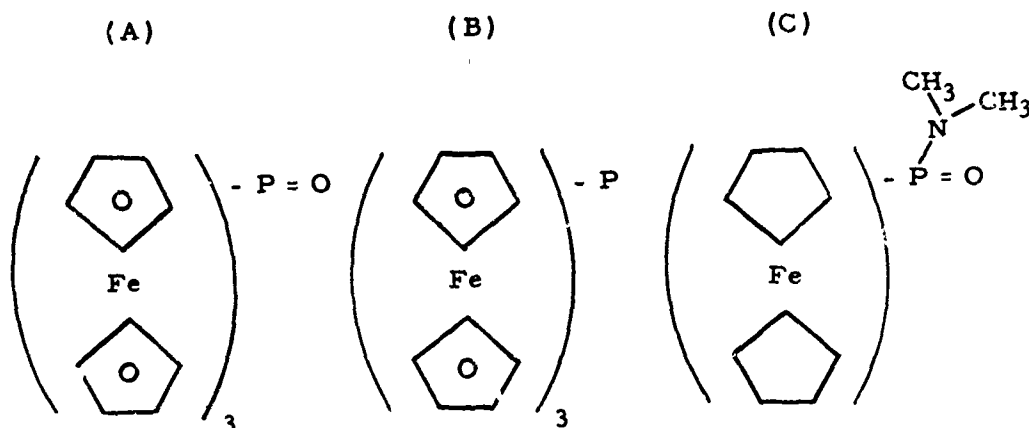
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Pressure DTA of mixtures of these materials, ferrocene and butyl ferrocene with ammonium perchlorate revealed the following correlation:

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Material	Ease of Oxidation	AP Exotherm Peak Temperature
Fe_2O_3	5	373
Ferrocene	2	260
Butyl Ferrocene	1	240
(A)	4	332
(B)	3	329
(C)	4	337

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Therefore, the easier the iron compound (ferrocene derivative) is to oxidize, the earlier the decomposition of ammonium perchlorate occurs. It should be pointed out that no attempt has been made to correlate the intensity of the exotherm in this series.

(U)   (12) Oxidizer Deflagration in Presence of Catalyst

(U)   Studies were made in order to determine whether the heat generated from the oxidizer catalysis reaction and the oxidation of ferrocene and ferrocene derivatives is sufficient to induce deflagration of the oxidizer particles.

(C)   At slow heating rates (2 to 10°C/minute), mixtures of 10 parts of ammonium perchlorate and 1 part ferrocene or butyl ferrocene will generally deflagrate at approximately 250 to 270°C. However, with higher concentrations of fuel (ferrocene or butyl ferrocene) the deflagration occurs at temperatures as low as 180°C.

(C)   Mixtures of 1 part of iron (III) oxide and 10 parts of ammonium perchlorate usually deflagrate at temperatures in the range of 300 to 340°C at the slower heating rates (2 to 10°C/minute).

(U)   (13) Effect of Iron Catalyst on Propellant Burning at
                           Atmospheric Pressure

(U)   If the efficacy of iron materials as catalysts in the burning rate of composite propellants is indeed due to more rapid gas phase reactions on the catalyst surface, then at atmospheric pressure, the effect of the catalysts on burn rate should be dampened. At atmospheric pressure the oxidizer decomposition flame zone is considerably thickened (from probably 5 to 50 microns to 200 to 500 microns). Therefore, from a given surface area of propellant, the area in which gas phase collisions can occur is considerably increased and the number of collisions is reduced. In addition, the exothermic catalysis reactions occur further from the surface resulting in less heat feed back to the surface. Observed increases in burn rate with iron catalysts should, therefore, be less than at pressures in the range of 200 to 1,000 psi.

(U)   A series of propellants containing 2 percent catalyst were prepared. The burn rates, as measured in strands at atmospheric pressure, are shown below:

	1	2	3	4
		Weight, %		
AP	74	74	74	74
HC/MAPO Binder	26	24	24	24
Fe_2O_3	--	2	--	--
Ferrocene	--	--	--	2
Butyl Ferrocene	--	--.	2	--
Burning Rate at Atmospheric Pressure	0.0579	0.0645	0.0608	0.0586

(C)   The observed 8 to 10 percent increase in burn rate at atmospheric pressure indicates that the catalysts are much less effective at 1 atmosphere of pressure than at 13 to 100 atmospheres.

(C)   It should be pointed out that these results could, in addition to the conclusion drawn, indicate that at atmospheric pressure the gas phase reactions do not occur close to the surface and in fact may be different in regard to mechanism from those occurring at normal operating pressure.

(U)   (14) Effect of Iron Oxide on Substituted Ammonium
                                 Perchlorate Decomposition

(U)   The following experiment was conducted in order to gain insight into the question of which gaseous decomposition reaction is catalyzed by iron containing compounds in the thermal decomposition of ammonium perchlorate. It was felt that the thermal decomposition of tetraethylammonium perchlorate (TEAP) would not produce perchloric acid as a product. The extraction of a proton from the ethyl group, which would be required to form the acid, is energetically unfavorable. Therefore, if iron oxide effects a more rapid decomposition of tetraethylammonium perchlorate, then the postulation that iron compounds effect a more rapid and efficient decomposition of anhydrous perchloric acid is in some doubt.

(U)   In addition, it was felt that a compound such as triethylammonium perchlorate, where a proton can be extracted, would exhibit a lower decomposition temperature if the postulation is correct. The proposed initial decomposition steps for ammonium perchlorate, tetraethylammonium perchlorate and triethylammonium perchlorate are summarized below.

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1) $NH_4ClO_4 \longrightarrow HClO_4 + NH_3$

2) $(C_2H_5)_4NClO_4 \longrightarrow C_2H_5ClO_4 + (C_2H_5)_3N$

3) $(C_2H_5)_3HNClO_4 \longrightarrow HClO_4 + (C_2H_5)_3N$
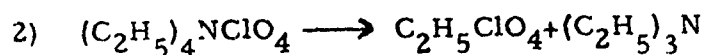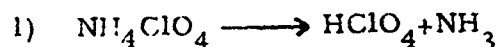
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(U)   A sample of the tetraethylammonium perchlorate was obtained com-
mercially and a sample of the triethyl substituted ammonium perchlorate was
prepared by neutralization of perchloric acid with triethylamine. The DTA of
these two compounds alone and in mixtures with 5 percent iron (III) oxide ex-
hibited the expected result (Figure 28); e.g., the thermal decomposition tem-
perature of the tetraethyl substituted compound was not affected by iron oxide
whereas the triethylammonium perchlorate exhibited the same effect as does
ammonium perchlorate. These experiments are strong indications that the
more efficient decomposition of perchloric acid in the presence of iron (III)
oxide is the probable rate controlling mechanism.

(U)   b.   Task B - Iron Catalysts Effects on Binder Composition

(U)   The study of the decomposition of binders and the effect of this pryoly-
sis on burning rate of composite propellants has long been neglected. The
decomposition products of the pyrolysis reaction are not known. The fact
that ferrocene and ferrocene derivatives have been shown to be excellent
combustion catalysts for hydrocarbons has placed even more emphasis in
this mechanistic effect of ferrocene on binder pyrolysis and to elucidate the
basic pyrolysis mechanism of polybutadiene polymers.

(U)   (1) Binder Pyrolysis

(U)   Several gumstocks were made from HA and HC polymers with varied
curing agents. The basic formulae for these two polymers are as follows:
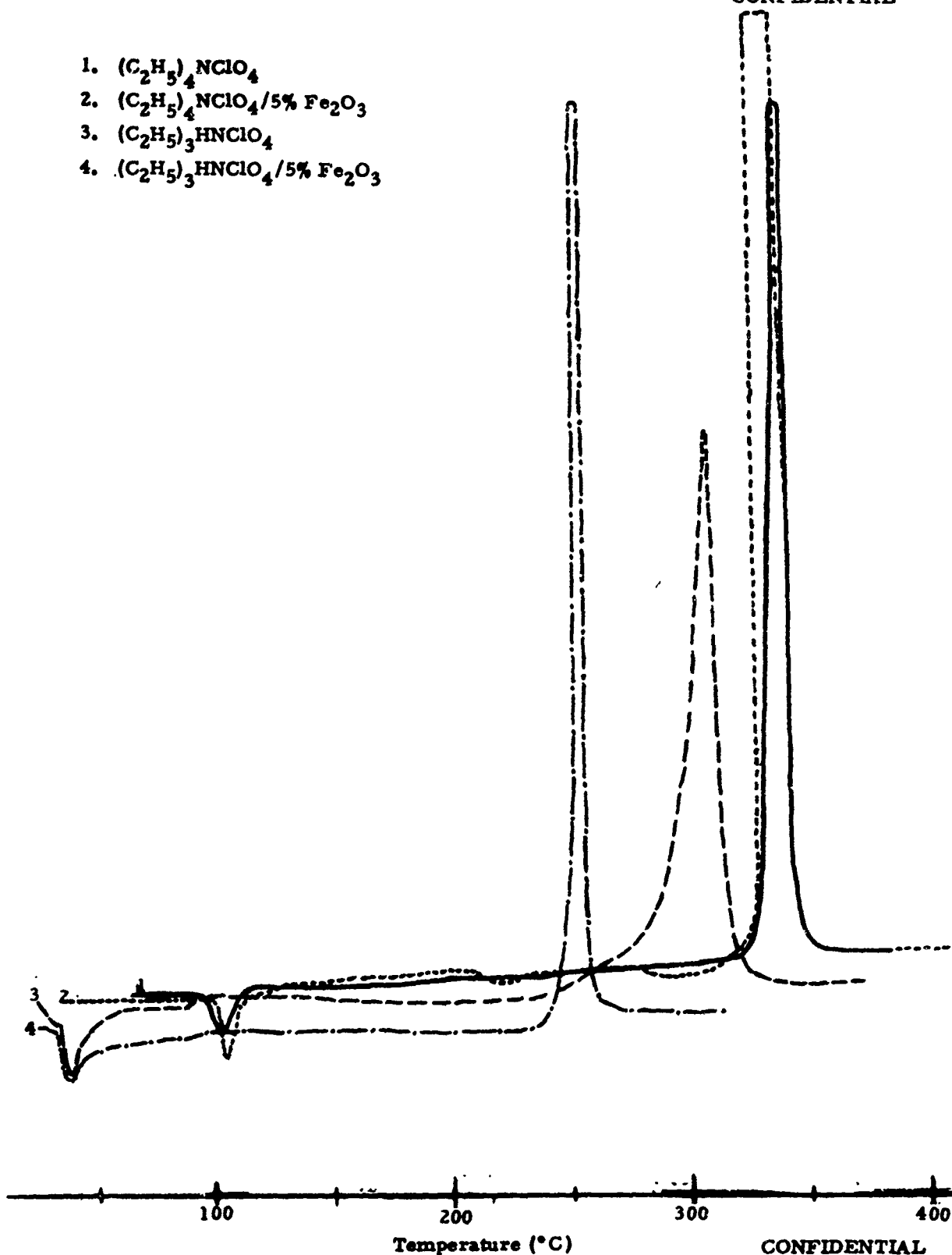
Figure 28. DTA of Tetraethylammonium Perchlorate and Triethyl
(Substituted for Ammonium Perchlorate).

HA (random carboxyl)

$$H - (CH_2 - CH = CH - CH_2)_x - (CH_2 - CH)_y - (CH_2 - CH)_2 - S - C_{12}H_{24}SH$$

with pendant groups: under first $(CH_2 - CH)_y$: $CH \parallel CH_2$ (as $\underset{CH_2}{\overset{CH}{|}}$); under $(CH_2 - CH)_2$: C, O, O, H (as $\underset{H}{\overset{C}{\underset{}{\overset{O}{\underset{O}{|}}}}}$)

HC

$$HOOC - CH_2 - CH_2 - CH_2 - (CH_2 - CH = CH - CH_2)_x - (CH_2 - CH)_y - CH_2 - CH_2 - CH_2 COOH$$

with pendant group under $(CH_2 - CH)_y$: $\underset{CH_2}{\overset{CH}{\underset{\parallel}{|}}}$
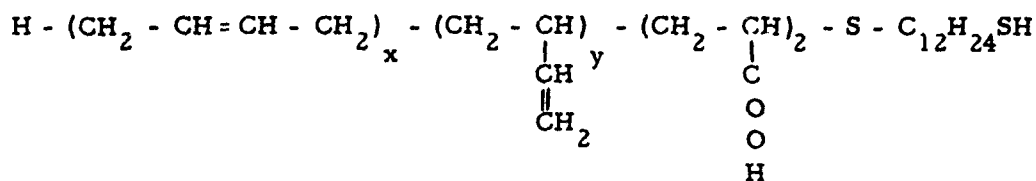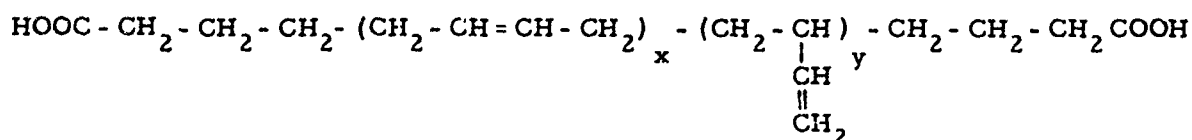
(U)   The HA polymer was cured with a difunctional epoxide, Bis Phenol-A[5], and the HC plymer was cured with MAPO[6] in one case, and a mixture of MAPO and ERLA-2795[7] in another.

(C)   Differential thermal analyses of all three gumstocks revealed a broad exotherm peaking at 372°C (Figure 29). The initial rise in heat release in the gumstocks containing an epoxide in the cure system can be attributed to the post cure reaction of the epoxide, which is characteristic of such systems. The fact that the exotherm is at 372°C for all gumstocks indicates that the heat release is related to the butadiene moiety and more specifically the double bond. As may be seen on Figure 30, a TGA on HC/MAPO gumstock indicates that no weight loss is associated with the exotherm at 372°C. It has thus been postulated that the exotherm is attributable to a further polymerization through the double bond of the butadiene moiety. Immediately following this exotherm, volatilization occurs and thermocouple contact is no longer maintained. (Note irregularity in curve following the exotherm.)

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5.   Brand name for a proprietary product; para,para'-isopropylidenediphenol supplied by The Dow Chemical Company, Midland, Michigan.

6.   tris   1-(2-methyl)aziridinyl   phosphine oxide, a trifunctional imine; product of Interchemical Corporation, New York, New York.

7.   Trifunctional epoxide: product of Union Carbide Corporation, New York, New York.
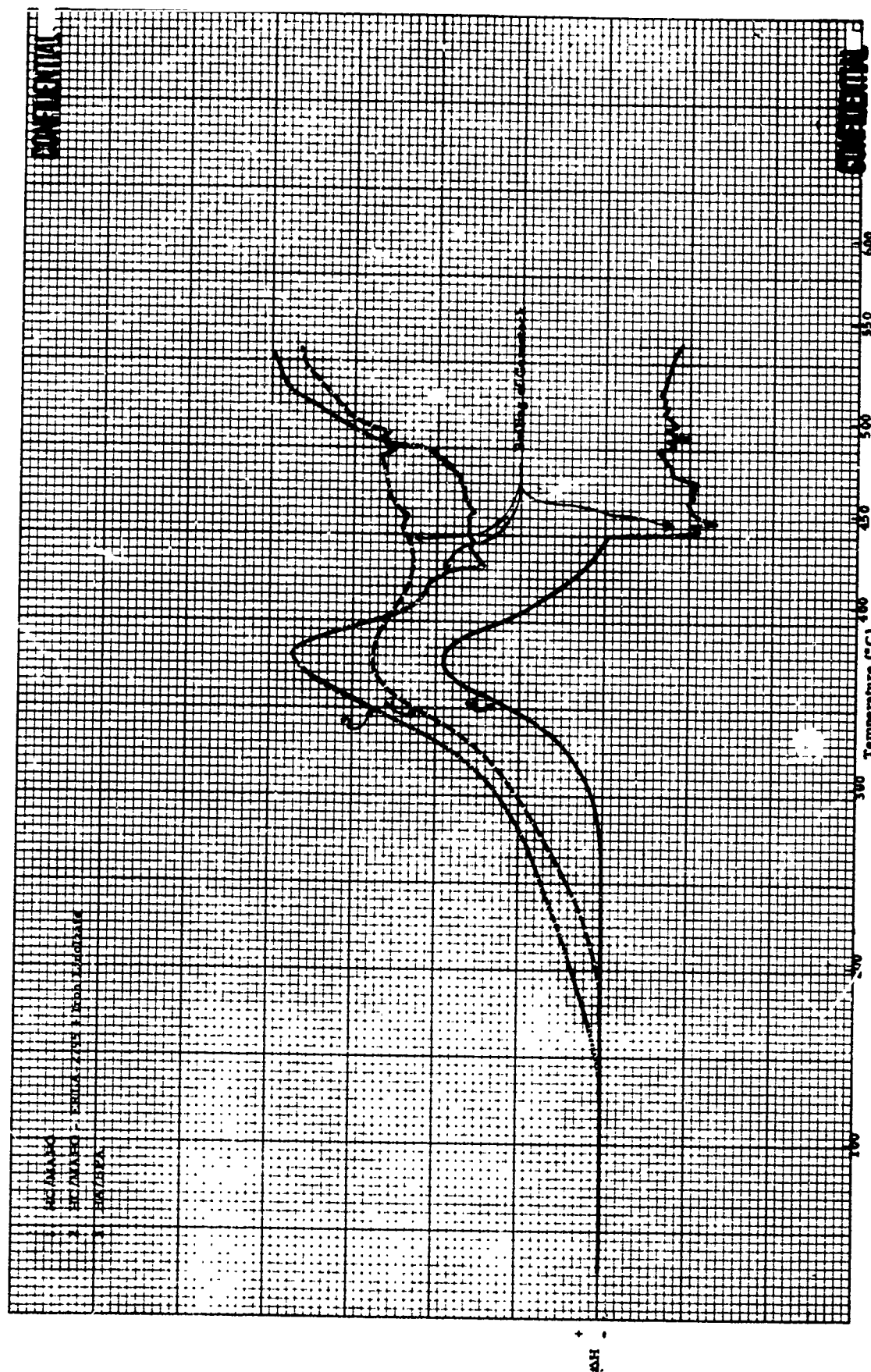
Figure 29. DTA of Gumstocks Under 200 psig N_2.
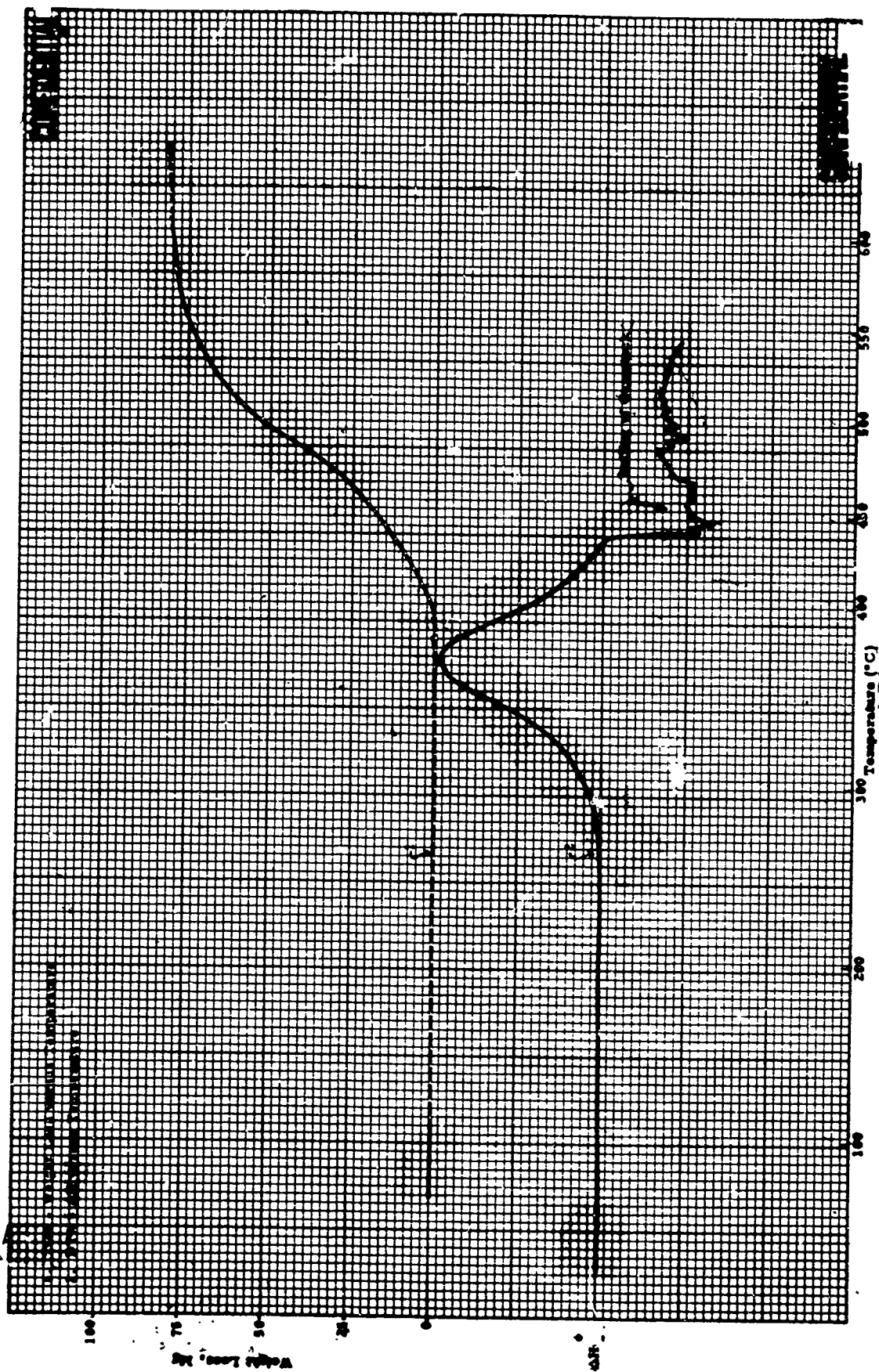
Figure 30. TGA (Curve 1) and DTA (Curve 2) of HC/MAPO Gumstock.

(U)   (a) Binder Pyrolysis and Decomposition Catalysts

(C)   Several experiments have been run in order to determine if ferrocene
or ferrocene derivatives effect a more rapid decomposition of polybutadiene
type polymers and cured rubbers. The TGA of mixtures of HA or HC polymer
with iron (III) oxide, ferrocene and butyl ferrocene exhibit weight loss of
polymer at the same temperature as that obtained with pure polymer; however,
prior weight loss occurs due to the volatilization of ferrocene or butyl ferrocene.
There is no indication of more rapid pyrolysis of polymer or binder in the
presence of these iron catalyst.

(C)   Differential thermal analysis of these mixtures substantiate the obser-
vations from the TGA. As a base of reference, the DTA of HC/MAPO gum-
stock in nitrogen and in air (800 psig) is shown on Figure 31. The only notice-
able differences are the preliminary exotherms under air which can be attri-
buted to homopolymerization of unreacted MAPO followed by oxidation and
the increase in exothermicity of the double-bond polymerization reaction in
the gumstock. The increase in heat release could possibly be attributed to
minor air oxidation occurring during this reaction.

(C)   The effects of Fe_2O_3, ferrocene and butyl ferrocene are depicted on
Figure 32. The exotherms at 130°C in the case of butyl ferrocene and at
160°C for ferrocene can be attributed to oxidation of these materials. The
exotherm at 305°C with butyl ferrocene and HC gumstock is unexplainable.
This peak is the only indication of possible binder decomposition at a tempera-
ture lower than that obtained with pure gumstock.

(C)   The effect of pressure upon the DTA of a mixture of HC/MAPO gum-
stock and ferrocene (ratio of 7/1) is shown on Figure 33. The peak corres-
ponding to ferrocene oxidation is more accentuated at 800 psi than at 200 psi.
The same conditions are shown with a similar experiment with HC/MAPA gum-
stock and butyl ferrocene (Figure 34).

(C)   A series of DTA's were run on gumstocks containing catalysts in order
to ascertain whether the exothermicity of polymerization is increased in the
presence of catalyst and whether preliminary decomposition occurred in the
presence of the catalysts. As shown on Figure 35, the heat release from
the polymerization is increased in the presence of ferrocene and butyl ferrocene
and is basically unchanged in the presence of iron (III) oxide. Such an obser-
vation is supported by the fact that ferrocene is known to be a combustion
catalyst for hydrocarbons. However, in no case was preliminary decomposi-
tion (volatilization) noted when catalysts were incorporated into the gumstocks.

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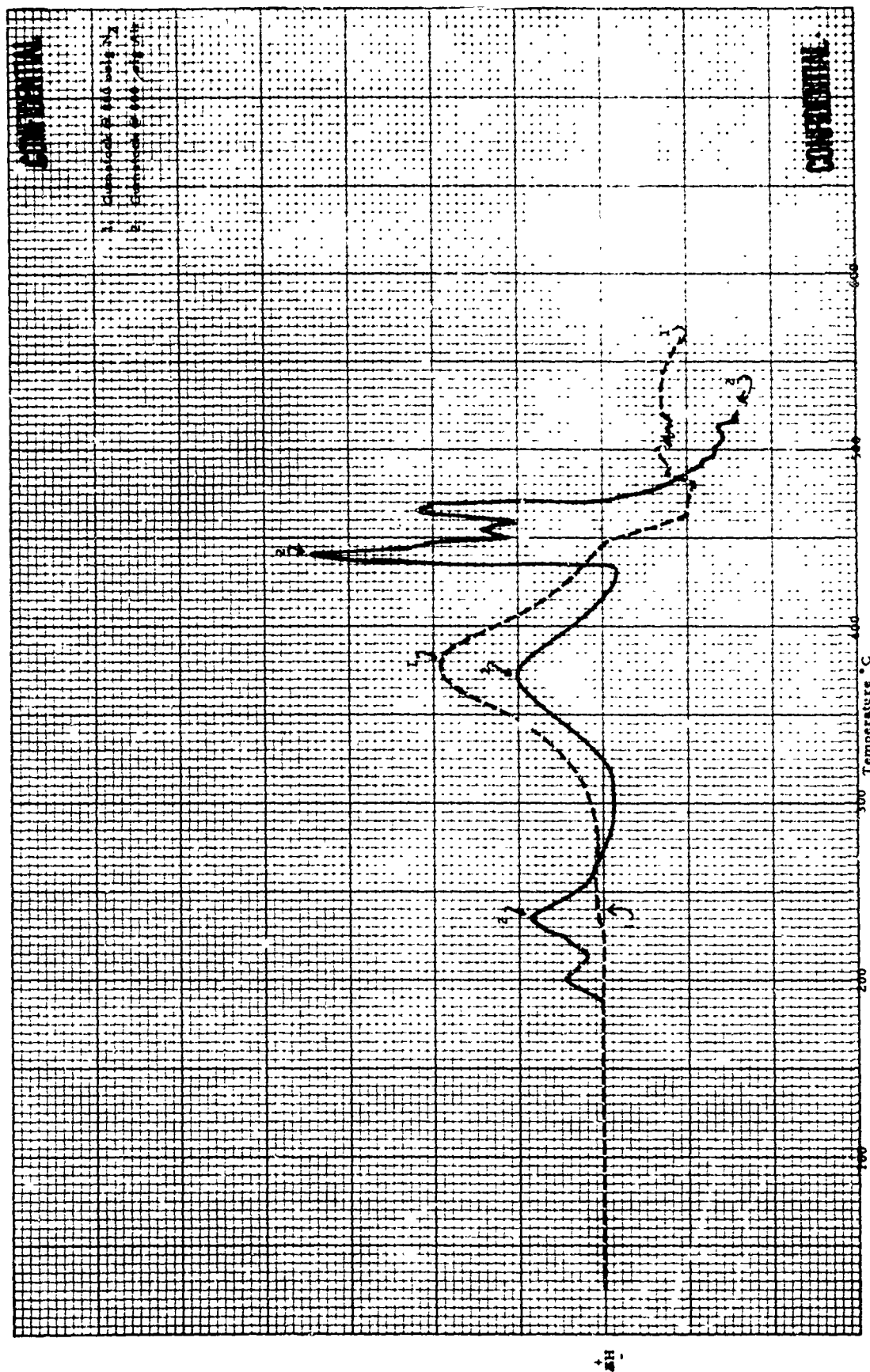
Figure 31. DTA of HC/MAPO Gumstock Conducted at 800 psig of N_2 versus Air.
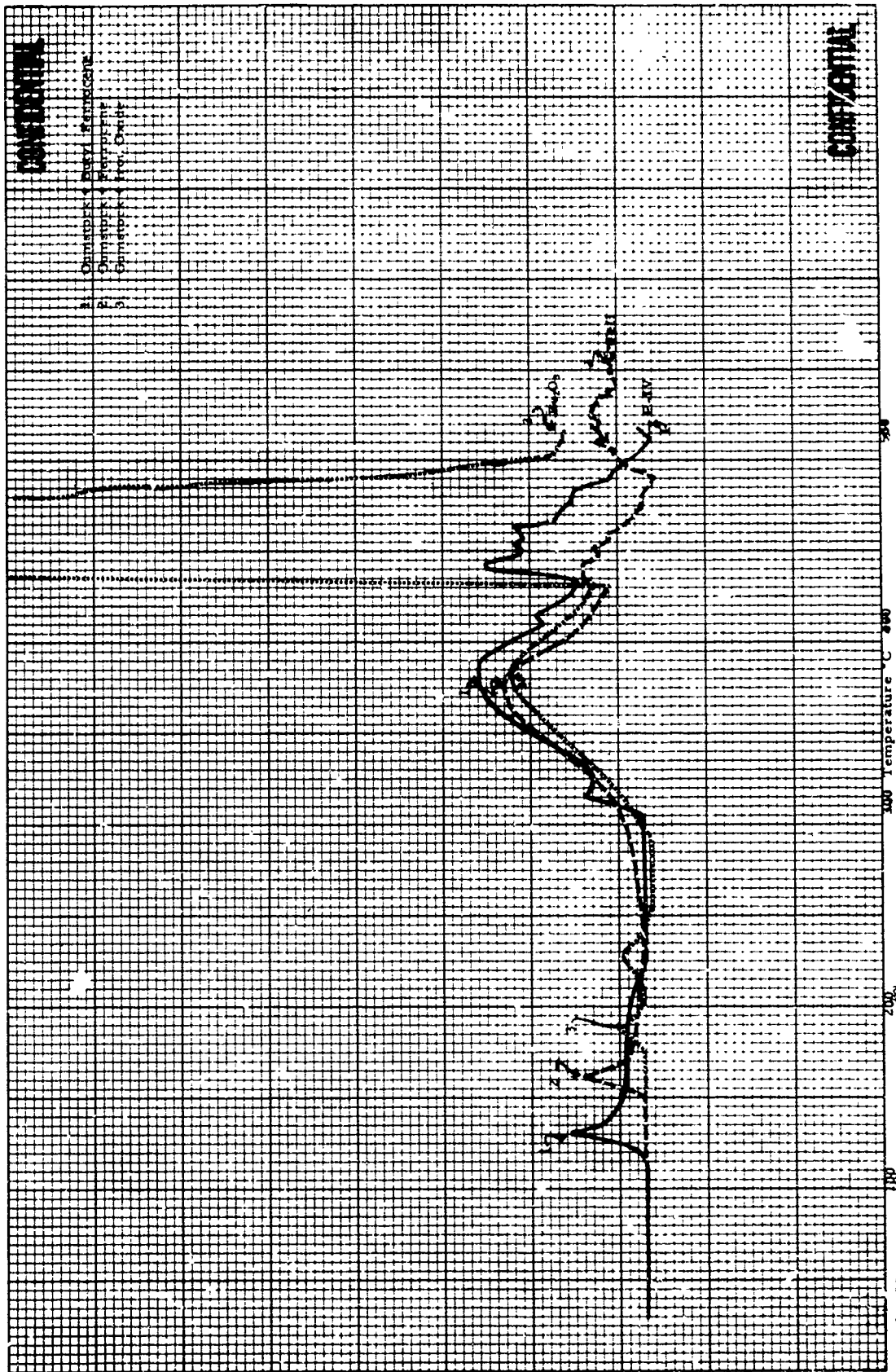
Figure 32. DTA of HC/MAPO Gumstock with Various Catalysts Conducted at 800 psig of Air with a 7/1 Ratio of Gumstock/Catalyst.
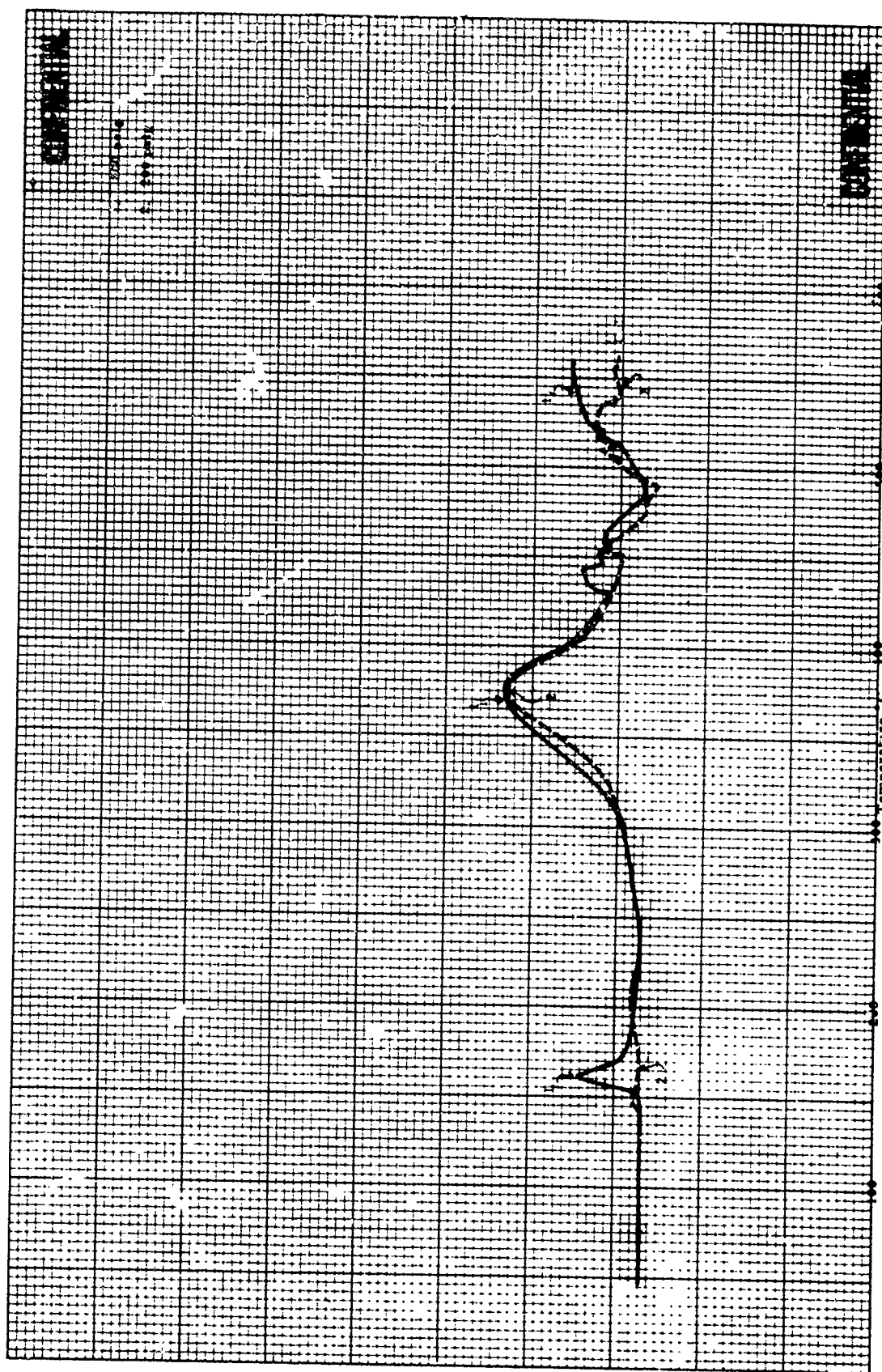
Figure 33. DTA of HC/MAPO Gumstock, Catalyzed with Ferrocene, Conducted at 200 and 800 psig of Air.
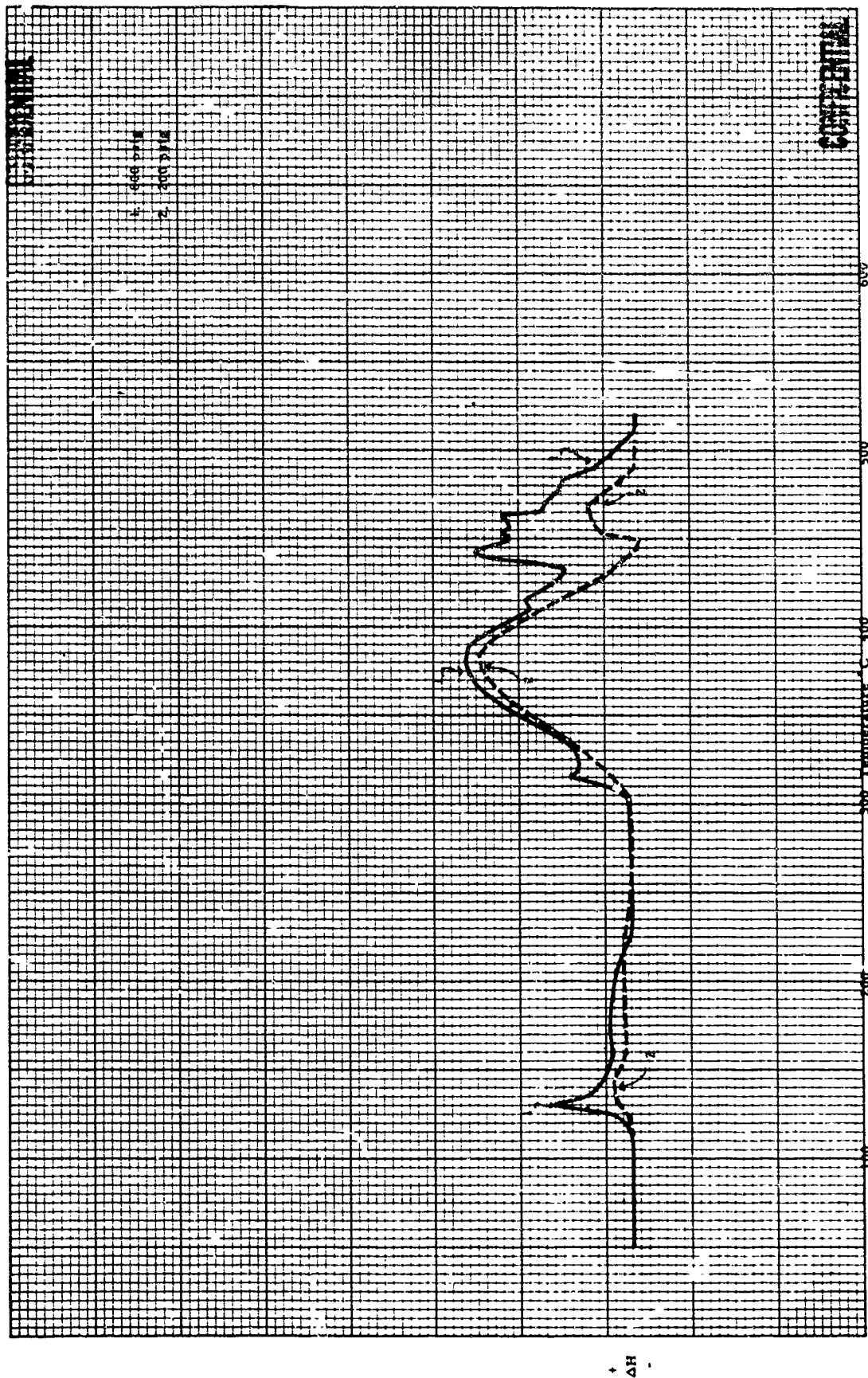
Figure 34. DTA of HC/MAPO Gumstock, Catalyzed with Butyl Ferrocene, Conducted at 200 and 800 psig of Air.

68
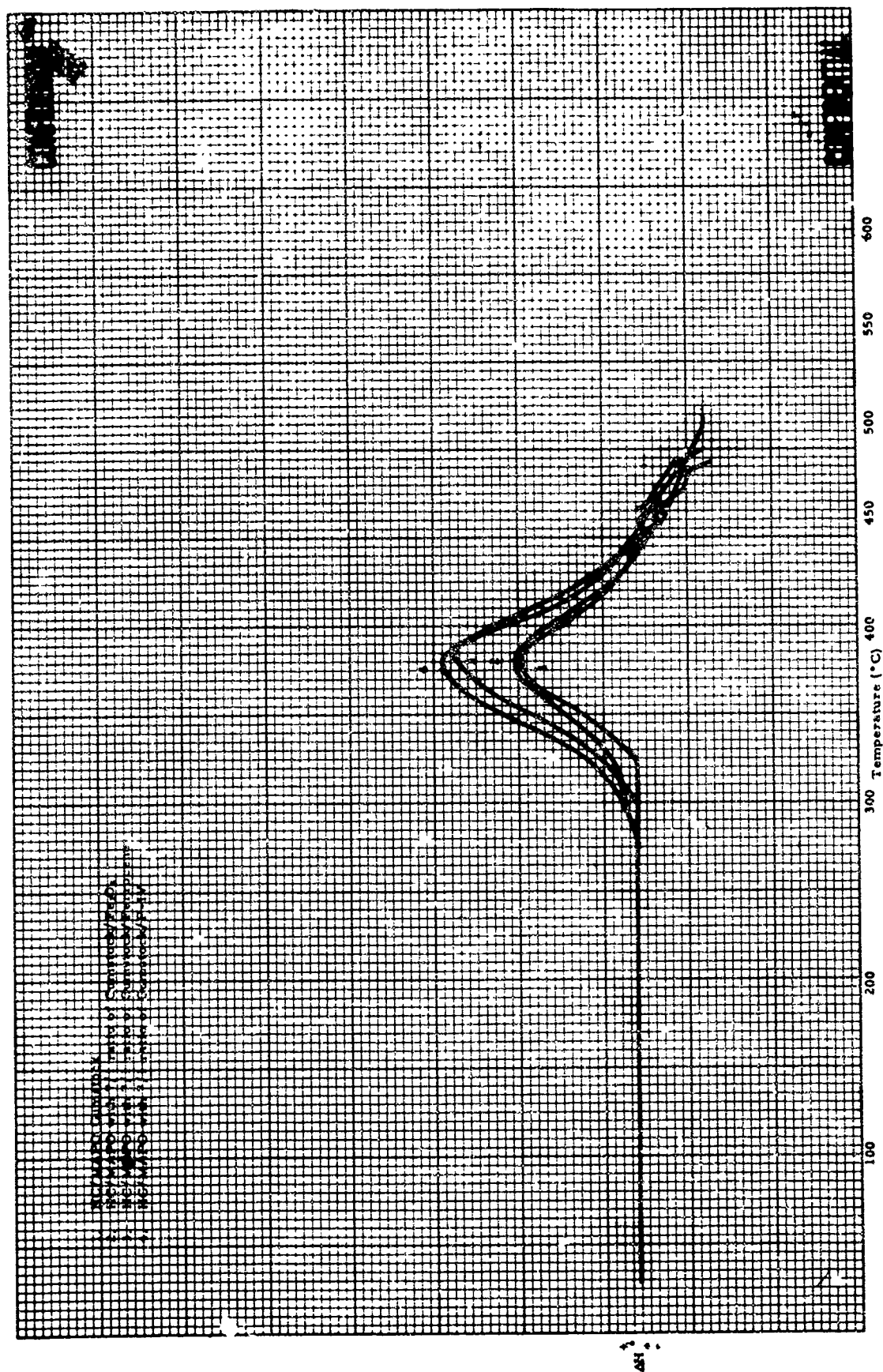
Figure 35.   DTA of Catalyzed and Uncatalyzed HC/MAPO Gumstock Conducted at 200 psig (N_2 Atmosphere).

(U)   (b) Effect of Pressurized Air on the Thermal Decomposition
            of HC/MAPO Gumstocks

(C)   Sample of HC/MAPO gumstocks were subjected to DTA under 200 and
800 psi of air (Figure 36). Fairly sharp exothermic peaks occur at 200 to
250°C at the higher pressure with a resultant decrease in the over-all inten-
sity of the binder polymerization exotherm. These initial exotherms have
been attributed to the homopolymerization of MAPO, followed by thermal
decomposition of the MAPO, as indicated by a separate DTA on pure MAPO
(Figure 37).

(U)   (c) Effect of Catalysts Upon the Thermal Decomposition of
            HC/MAPO Binders Under Pressurized Air

(C)   Gumstocks of HC/MAPO containing Fe_2O_3, ferrocene, and butyl
ferrocene were thermally decomposed under 200 and 800 psi of air. Oxidation
of ferrocene and butyl ferrocene are apparent at 125 to 150°C and MAPO
polymerization occurs in the presence of Fe_2O_3 at 190 to 230°C. An explana-
tion for the other exotherms is not available at this time.

(U)   (d) Effect of Catalyst Upon Binder Pyrolysis

(U)   Of primary importance in determining the effect of iron con-
taining catalysts on propellant burn rate mechanism is knowledge of
the decomposition of the binder. In order to ascertain the effect of
the catalyzed binder decomposition on the burning rate of propellants,
potassium perchlorate was substituted for the ammonium perchlorate
normally used in a propellant. All other propellant ingredients re-
mained constant. Potassium perchlorate was chosen as the oxidizer
to replace the ammonium perchlorate since past tests had shown
that iron was ineffective in accelerating the decomposition rate of
potassium perchlorate; thus, any increase in burn rate noted could be
attributed to increased binder pyrolysis rate.

70
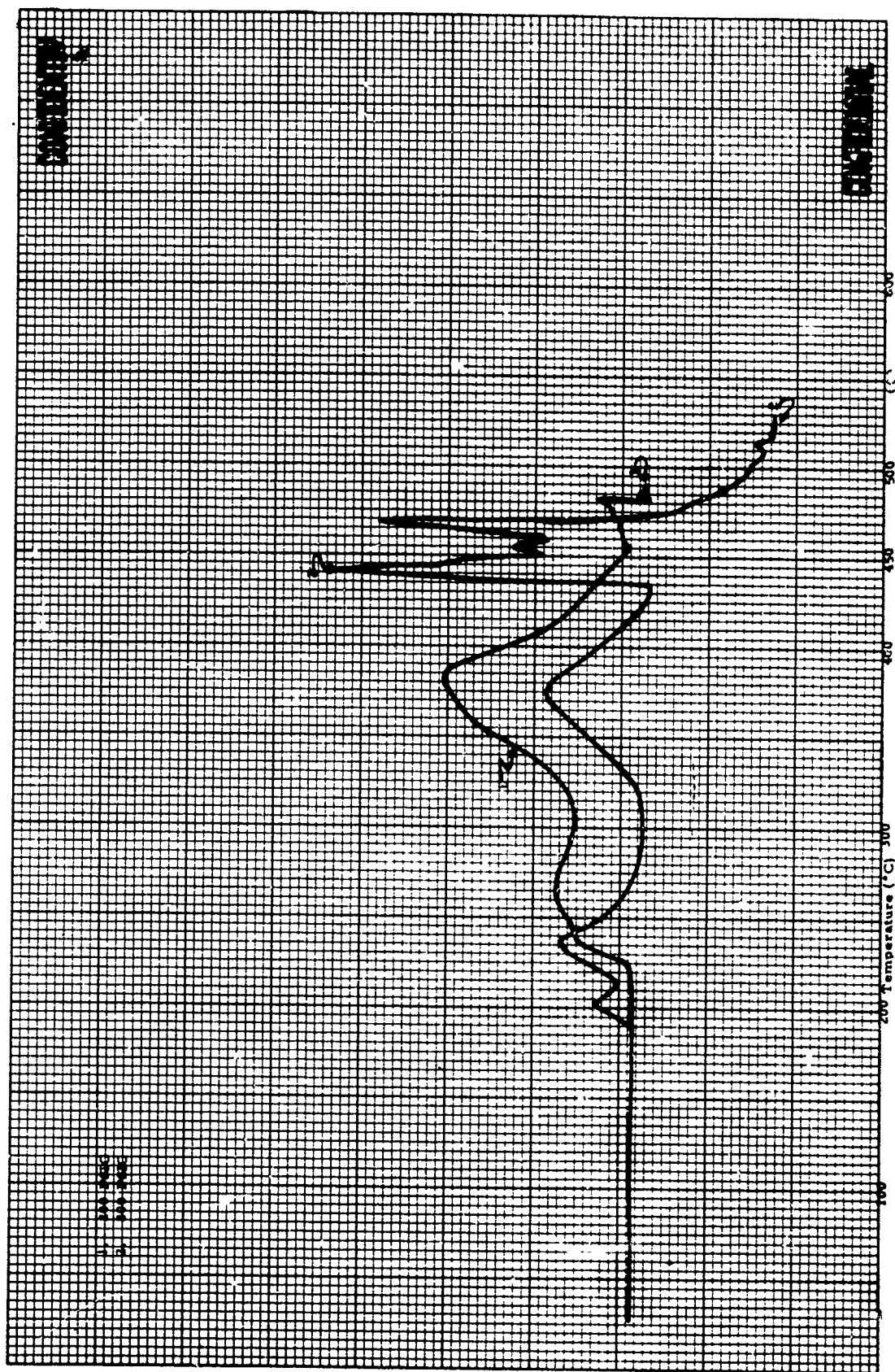
Figure 36. DTA of HC/MAPO Gumstock Conducted at 200 and 800 psig of Air.
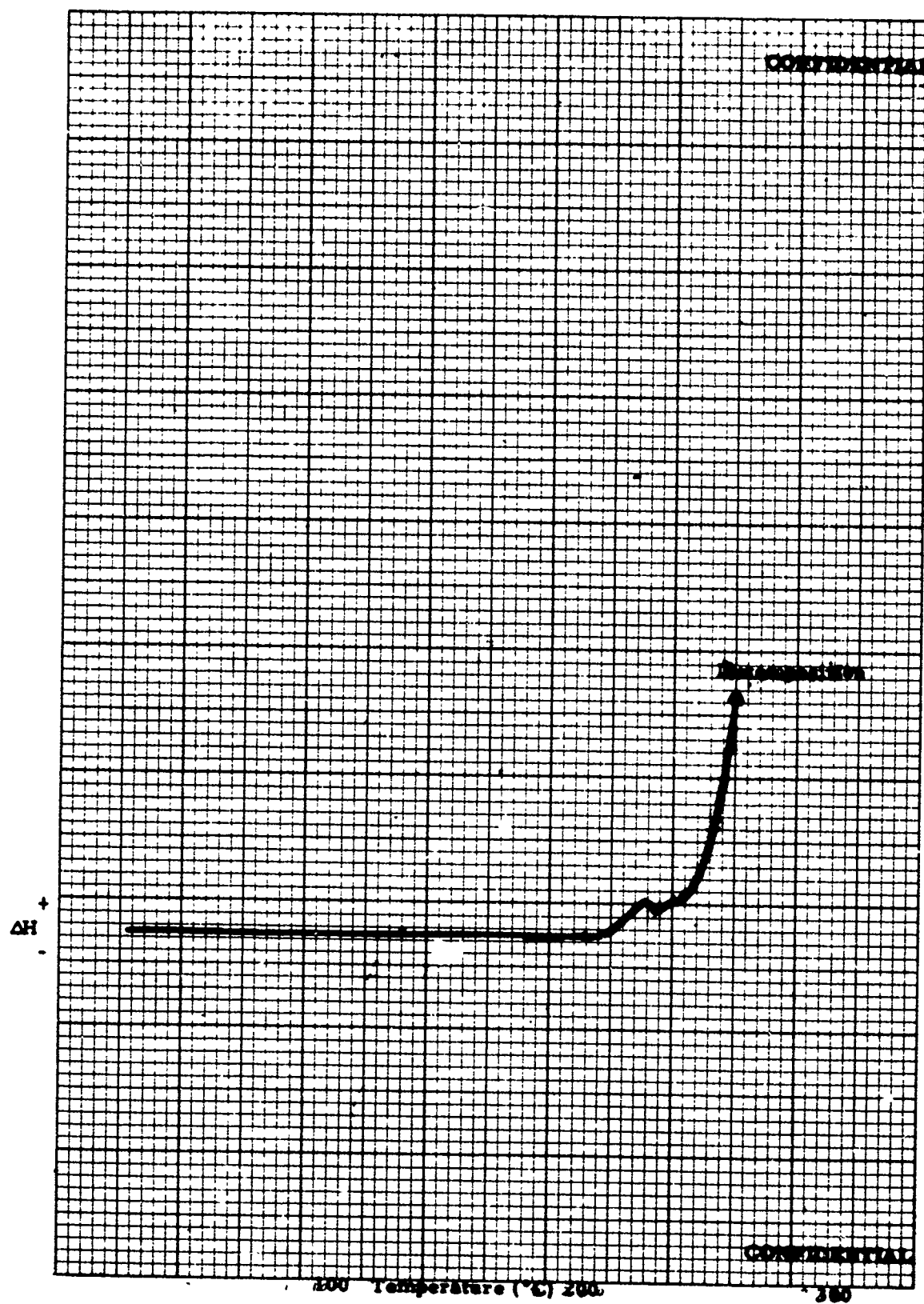
Figure 37.   DTA of MAPO Conducted at Atmospheric Pressure.

(C)   Three propellants were prepared: one was non-catalyzed
and the remaining two were individually catalyzed with ferrocene and
butyl ferrocene. Propellant strands were combusted at 14.7 and 500
psig from each of the three propellants with the results shown on
Figure 38. It is obvious from these results that ferrocene or butyl
ferrocene do not effect binder pyrolysis. The small, almost
negligible increase in propellant burning rate was derived from the
fact that the materials were volatile, had a low enough molecular
weight to be consumed in the primary flame zone, and had high
enough heat of combustion to add heat to the zone, thus slightly in-
creasing the binder pyrolysis.

(U)   c.   Task C - Iron Catalysts Effects on Aluminum Combustion

(U)   The possibility that either iron oxide or ferrocene will react with
hot molten aluminum in an oxidizing atmosphere has not been considered on
combustion studies of solid propellants. It is known that under certain con-
ditions a Thermit reaction can occur between iron oxide and aluminum. Such
a reaction is very exothermic and would add substantial quantities of heat
to the surface.

(U)   In order to determine if the reaction between aluminum and iron (III)
oxide (Thermit reaction) can be initiated and contribute substantial heat to
the reacting burning surface of propellant, preliminary experiments con-
cerning initiation temperature and concentration of ingredients were run.

(C)   Two-gram samples of aluminum were exposed to a low temperature
($\sim 700°C$) flame for one minute periods and only two or three particles would
ignite. Naturally, the iron (III) oxide was inert to the same conditions. How-
ever, mixtures of Fe_2O_3 aluminum powder (1 - 12 to 1 - 3) ignited spontaneo-
usly with application of the flame.

(C)   Forced hot air (500°C) would not ignite the mixtures and the coolest
flame that could be obtained was approximately 700°C. The mixture was
readily ignitable. This gap in temperature could not readily be bridged.
Therefore, the answer to the desired question was not obtained experimentally.
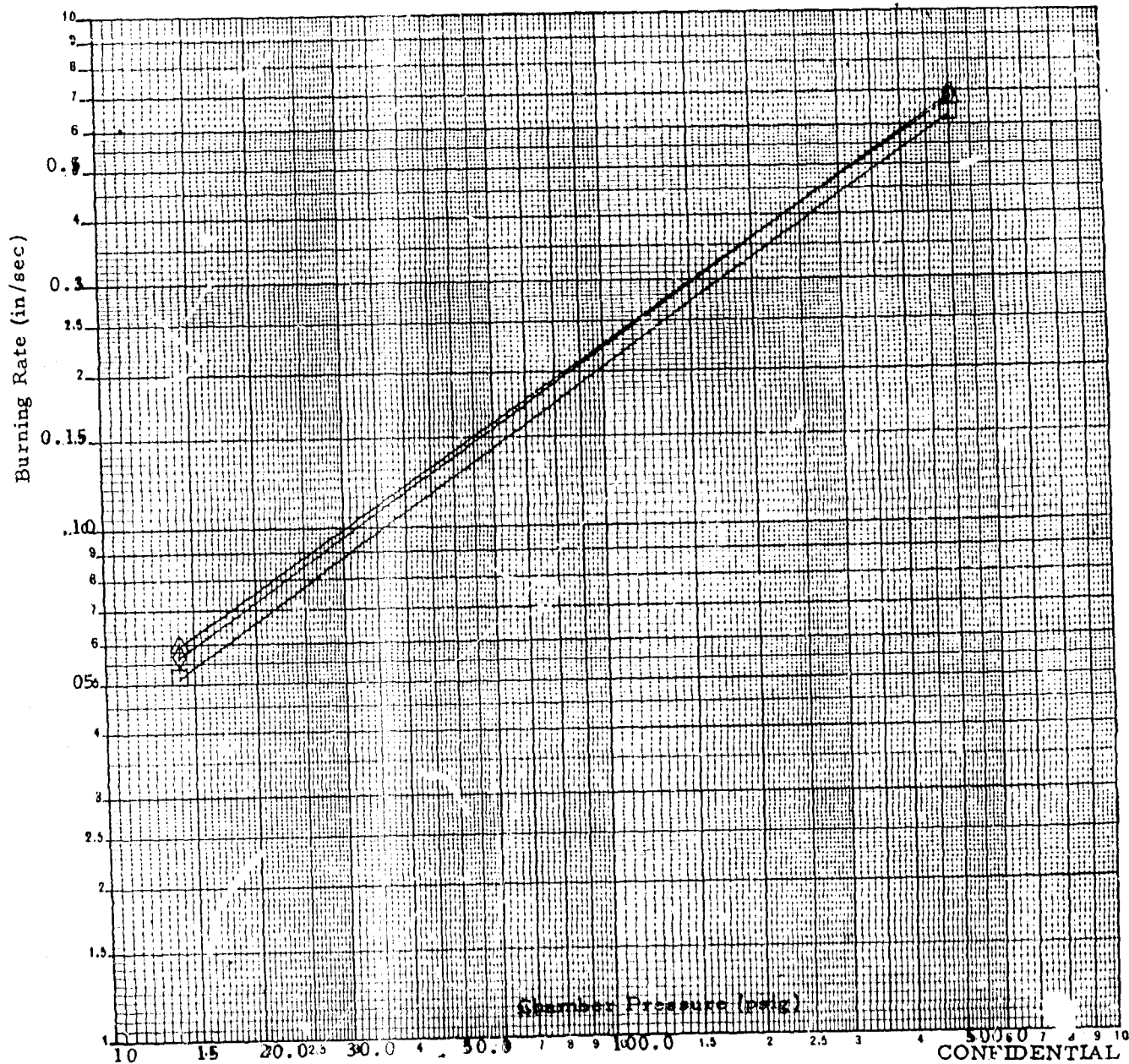
Figure 38. Burning Rate versus Pressure Relationship for an 84 Percent Total Solids Propellant Containing $KClO_4$ in Catalyzed and Non-catalyzed Systems.

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(C) Due to the fact that it was experimentally determined that iron containing materials resulted in approximately the same burn rate increases whether used in aluminized or non-aluminized propellants, this area of work was no longer pursued.

(U) 3. <u>Phase III - Studies of Catalysts With Composite Propellants</u>

(U) a. <u>Propellant Studies</u>

(U) (1) <u>Effect of Occluded Iron Oxide</u>

(U) In order to try to further answer the question as to whether solid phase catalysis does occur, samples of ammonium perchlorate and iron oxide were cocrystallized (occluded) in order to obtain maximum contact of oxidizer and catalyst. Following thorough drying, the crystals were screened into a narrow particle size range. A sample of pure ammonium perchlorate was subjected to the same recrystallization (without iron oxide present) and screening processes. The occluded sample was analyzed for Fe_2O_3 content. Two propellant samples were made containing the Fe_2O_3 occluded ammonium perchlorate and the pure ammonium perchlorate with the same amount of Fe_2O_3 added to the mix as is contained in the occluded sample. Burn rates were measured at 500 psi.

(U) The formulations manufactured and tested are shown below:

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Component	TP-H8041 + Fe_2O_3	TP-H8041 (Mod)
AP	68.00	68.00
Al	16.00	16.00
HC/MAPO	15.05	15.05
Fe_2O_3	0.95	0.95 (occluded)

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The measured burn rates, based on an average of 6 strands burned for each formulation, are as follows:

	Burning Rate at 500 psi (in/sec)
Fe_2O_3 (mixed) propellant	0.341
Fe_2O_3 (occluded) propellant	0.332

(C)   The insignificant increase (2-1/2 percent) in burn rate again points to the fact that contact between catalyst and oxidizer is not a controlling parameter in the burn rate mechanism.

(U)   (2) Comparison of Iron Oxides Prepared by Different Techniques

(C)   In order to determine what differences exist between "as received" iron oxide and iron oxide prepared from the oxidation of ferrocene, a series of burn rates were measured in propellants containing Fe_2O_3 prepared in different ways (0.43 grams of Fe_2O_3 is available from the oxidation of 1 gram of ferrocene). The following catalyst variations were studies:

1.   1 percent ferrocene
2.   1 percent Fe_2O_3 (as received)
3.   0.430 percent Fe_2O_3 prepared from the Parr
       bomb combustion (7 atm O_2) of ferrocene
4.   0.430 percent Fe_2O_3 (prepared by oxidizing ferrocene
       in air followed by calculation of the resultant Fe_2O_3
       at 1400°F for 1 hour.

The results of the burn rate measurements are as follows:

Catalyst Variation	Burning Rate at 500 psi (in/sec)
1	0.381
2	0.342
3	0.270
4	0.346

(U)   The following conclusions can be drawn from these data:

(C)   1.   Basically, the burn rates obtained from 1 percent ferrocene (catalyst variation 1) and 0.430 Fe_2O_3 (catalyst variation 4) are very similar.   They should be the same if one can consider that air oxidation of ferrocene followed by calcination would produce the same specific surface Fe_2O_3 as combustion in a propellant would accomplish.

(C)   2.   Catalyst variation 3 exhibits low rate because of agglomeration of the Fe_2O_3 prepared in that manner.

(C)   3.   The same rate is obtained with 1 percent "as received" Fe_2O_3 as with 0.430 percent Fe_2O_3 prepared from oxidation of ferrocene. This can simply be explained by the larger specific surface obtained from the latter technique.

(U)   b.   Analysis and Interpretation of Phases I - II Data

(U)   A critical examination of the burning process reveals three questions that must be answered before a catalysis mechanism can be postulated:

1).   Do solid phase catalysis reactions occur?

2).   If catalysis is not solid phase, what gas phase reactions are catalyzed by iron compounds?

3).   What is the effect of iron compounds upon binder pyrolysis?

(C)   As a result of Phases I and II experiments, considerable evidence exists that no solid phase catalysis reactions occur. Some of the pieces of evidence refuting solid phase catalysis are listed below:

(C)   1). Photographic evidence of no increased decomposition rate of ammonium perchlorate when in contact with iron (III) oxide.

(C)   2). Ammonium perchlorate containing occluded iron (III) oxide does not result in a higher burn rate propellant than one in which a like amount of Fe_2O_3 is mixed into the propellant.

(C)   3). Similar particle sized iron (III) oxide of varying specific surfaces results in increased burn rate with increased specific surface of catalyst.

(C)   4). Analysis of partially decomposed ammonium perchlorate reveals the absence of reduced iron compounds and no change in the ammonium perchlorate.

(C)   5). Experiments in which mixtures of ammonium perchlorate and Fe_2O_3 were subjected to thermal gravimetric analysis revealed that if the iron oxide was layered on top of a sample of ammonium perchlorate, the decomposition rate was slightly more rapid than when the oxidizer and catalyst were premixed.

(C)   6). Iron catalysts exhibit only a very slight catalytic effect on the burn rate of composite propellants at atmospheric pressure. However, at 100 psi the effect is quite dramatic. Pressure should not affect a solid phase catalysis.

(C)   7). One gram of ferrocene results in 0.43 grams of iron (III) oxide upon oxidation. A sample (0.43 grams) of iron (III) oxide prepared by the oxidation of ferrocene resulted in approximately the same burn rate as 1.0 gram of ferrocene when incorporated into like propellant formulations.

(C)   Although conclusive evidence is not available for a gas phase catalysis, the presence of any solid phase catalysis reaction is felt to be remote based on the aforementioned experimental observations.

(C)   If gas phase catalysis does occur, then the question of what reaction would be catalyzed by iron (III) oxide is open for debate. It had been pre-supposed that more efficient decomposition of anhydrous perchloric acid was the result of the presence of catalyst. None of the experiments conducted during this program has refuted this postulation and several pieces of evidence have been made available which add credence to such a rate controlling reaction:

(C)   1). The initial decomposition step in the thermal decomposition of ammonium nitrate is similar to that for ammonium perchlorate; e.g., the formation of ammonia and the respective acid. The fact that Fe_2O_3 effects a more rapid decomposition of ammonium perchlorate and has little or no affect on the decomposition of ammonium nitrate is evidence that perchloric acid-catalyst interaction is important.

(C)   2). The presence of iron (III) oxide in admixture with potassium perchlorate does not result in a significant lowering of the decomposition temperature of potassium perchlorate. This would be predicted since perchloric acid is not a decomposition product of potassium perchlorate.

(C)   3). Dramatic increases (tenfold) in the decomposition rate of anhydrous perchloric acid on iron oxide as well as other microfine particles have been noted.

(C)   4). Iron oxide lowers decomposition temperature of ammonium perchlorate. Iron oxide lowers decomposition temperature of triethylammonium perchlorate. Iron oxide does not affect the decomposition temperature of tetraethylammonium perchlorate. Therefore, in compounds where perchloric acid is the initial primary decomposition product, lowering of the decomposition temperature is a result of the presence of iron (III) oxide.

(C)   In regard to the question of whether the particular iron compounds studied will affect the pyrolysis rate or decomposition temperature of hydrocarbon based binders, it can be said that no experimental evidence could be obtained which would indicate that the presence of the iron compounds in cured or uncured polymer systems affects the pyrolysis rate or decomposition temperature.

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(U) c. Postulation of a Mechanism

(U) A review of the experimental data resulting from this program as well as that data generated since 1951 on the effects and ramifications of the incorporation of varied iron containing compound into ammonium perchlorate based composite propellants has resulted in a postulation as to why burn rate is increased when such compounds are present. It should be pointed out that the following postulation is one which best accounts for the phenomena encountered in the art of increasing the burn rate of composite propellants. The postulated sequence of events is as follows:

(C) It is known that if the oxidizer deflagration reactions react equilibrium at 1,000 psi, a temperature of approximately 1200°C could be attained. The burn rate of a given propellant, therefore, will be dependent upon how near to the equilibrium temperature the oxidizer decomposition reactions approach at a given distance (less than 10 microns) from the regressing surface. The higher the temperature attained very close to the surface, the more the heat feed back to the surface and therefore the more rapid the surface regression rate.

(C) The oxidizer, under the influence of this oxidizer decomposition flame, decomposes initially into perchloric acid and ammonia. The rate of perchloric acid decomposition will then be the rate determining reaction in attaining the equilibrium temperature. The initial decomposition of perchloric acid proceeds via the formation of the hydroxyl and chlorate free radicals. It is felt that this reaction occurs more efficiently upon the surface of an iron oxide particle, thus resulting in higher temperature generated very close to the surface. As is the case in any catalytic reaction, there is a leveling off of catalytic effect with increasing sites for catalysis. Such is observed for propellants containing iron oxide.

(C) It should be pointed out that as far as burn rate is concerned, little if any effect on burn rate can be attributed to reactions occurring more than 10 microns from the surface. This is evident from the fact that variations in aluminum content (0 to 16 percent) have only a very slight effect upon burn rate. Therefore, flame temperature on the heat of oxidation of aluminum are not rate controlling functions.

(C) As far as ferrocene and other organic iron containing compounds are concerned, the iron (III) oxide resulting from the very rapid oxidation of these materials is of extremely small particle size and extraordinarily high specific surface, thus accounting for the increased burn rates attainable from the use of such compounds. In addition, the heat of oxidation of these materials serves as a further source of heat to the burning surface. Visual observation

of the oxidation of ferrocene reveals a reaction which appears similar to an explosion with expulsion of a multitude of microfine iron (III) oxide from the surface. Therefore, the use of organic iron compounds in composite propellants serves as a source of generation in situ of iron oxide particles, the particle size of which is much smaller than could be satisfactorily processed into a propellant.

(C)   The efficacy of iron compounds in the burning process is, therefore, felt to be a means whereby the temperature of the oxidizer flame zone within a few microns of the surface can be increased.

(U)   d.   <u>Mathematical Model to Study Rate Controlling Mechanism</u>

(U)   Analytical techniques that simultaneously consider the interactions between the gas phase and the solid phase are being developed to analyze the experimental data. The most complete physical models to explain the burning of ammonium perchlorate propellants deal primarily with the gas phase reaction (8, 9). Since most of the major effects on burning rate produced by changes in propellant ingredients can be explained in terms of the gas phase reaction, only a limited amount of analytical results have been obtained for the solid phase and surface reactions. Nachbar and Williams (10) examined relationships controlling the burning of semi-infinite slabs of ammonium perchlorate. Hermance (11) considered chemical reactions at the binder surface and ignored the diffusion process in the gas phase. Wenograd (12) has proposed that the primary heat release occurs at the propellant surface. While all the successful burning rate models considered the interaction between the flame zone and the solid phase, in all cases a number of limiting assumptions had to be made in order to get qualitative results. In the present analysis, the interactions between the gas phase, the ingredient interfaces, and the solid phase are more accurately accounted for. This is being accomplished by taking full advantage of the burning mechanism data that is being obtained and by solving a more general set of differential equations describing the heating, catalylic, and pyrolysis processes. In particular, the analysis will be directed at studying the individual composite propellant ingredients: binder, oxidizer, and burning rate catalysts.

(U)   In order for the analytical model to be successful, it must account for the following: the effect of oxidizer particle size on burning rate, the effect of chamber pressure on burning rate, and the mechanism by which burning rate catalyst enhances rate by causing the gas phase reaction to occur closer to the surface.

(U)   The equations to be solved have been considered by several investigators. In the most general form, diffusion and gas velocity should be considered in three dimensions; however, at this time, considerable increase in the understanding of how burning rate catalysts affect composite propellant burning can be obtained by solving the physical situation depicted in Figure 39. The important features of this figure are:

1). Temperature gradients are one-dimensional and normal to the burning surface.

2). Oxidize particles are spherical.

3). Increased reaction rates resulting from catalyst induced reactions are considered in the gas phase.

4). Surface temperature can either be prescribed or be determined from the heat balance at the surface.

5). Exothermic reactions produced by oxidative disintegration of ferrocene compounds.

6). Flame thickness is an independent variable to be calculated as a function of pressure and pyrolysis rate.

7). Effects of subsurface heating can be calculated.

8). Propellant is made up of a series of thermally thick layers which can be consumed sequentially.

9). Heat to the burning surface from the flame zone is calculated from the thermal conductivity and the temperature gradient in the gaseous phase.

10). Regression rate can either be prescribed or be calculated from a pyrolysis law.

11). Thermal properties may vary with temperature.

(U)   Figure 38 shows oxidizer being exposed to flame. The model is formulated in such a manner that binder and oxidizer are alternately exposed. The novel features of the model are that the general assumptions of a semi-infinite solid (steady-state burning), prescribed flame temperature, and no subsurface heating have been removed. In addition, quantitative results can be obtained to take advantage of laboratory experimental data that relate subsurface heat generation and pyrolysis rates to heating from the gaseous phase.
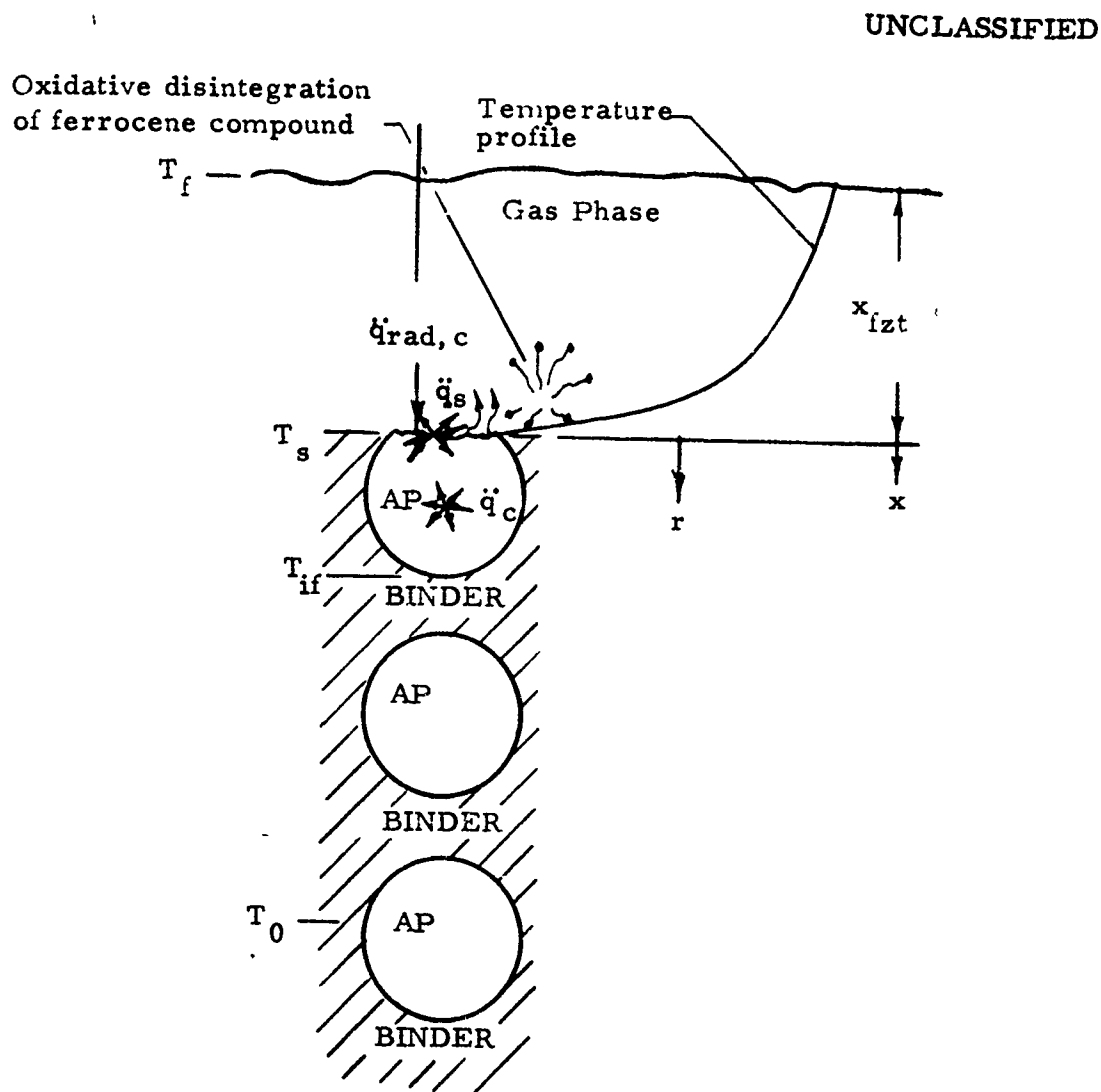
Figure 39. Physical Situation Considered by Mathematical Model

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(U)   The differential equations and the boundary conditions describing the individual thermal processes depicted by Figure 39 are derived from general heat transfer and chemical kinetics theory. For consistency with other published work, the terminology and nomenclature are similar to that used by Price (13) and by Johnson (10).

(U)   The equations for the interior of the solid phase are written as follows:

$$\begin{array}{ccccc} \text{I} & \text{II} & \text{III} & \text{IV} \\ \rho c \dfrac{\partial T}{\partial t} = \dfrac{\partial}{\partial x}\left(k \dfrac{\partial T}{\partial x}\right) + f(A)\dfrac{\partial T}{\partial x} + r \dfrac{\partial T}{\partial x} + \ddot{q}_i \end{array} \qquad (1)$$

The thermal properties vary with temperature. In Equation 1, the different terms have the following physical relationships:

I.   Time rate of energy accumulation. This term can be related to the temperature rise at a particular point.

II.   Energy transfer by thermal conduction in the solid.

III. Rate of energy convection due to motion of the surface (if a moving coordinate system is used).

IV.   Rate of heat generation.

(U)   The chemical rate of heat generation by an effective first order reaction is:

$$\ddot{q}_i = -Z_c e^{-\dfrac{E_c}{RT}} \qquad (2)$$

(C)   The temperature gradient through the gas phase is one of the dependent variables, and, accordingly, the surface boundary condition is:

$$-k_g \dfrac{\partial T}{\partial x}\Bigg|_{x = x_s} = -k_c \dfrac{\partial T}{\partial x}\Bigg|_{x = x_s} + \ddot{q}_s + \ddot{q}_{rad} \qquad (3)$$

$$T_g(x_s, t) = T_c(x_s, t)$$

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When Equation 4 is used in conjunction with Equation 1, the surface chemical reactions and the heats of phase change are considered. The regression rate at the surface is controlled by the linear pyrolysis law:

$$r = B_s T_s^{\beta_1} e^{-\frac{E_s}{R T_s}} \tag{4}$$

The usual initial conditions apply

$$T = T_0 \tag{5}$$

The boundary conditions at the interface between the layers of oxidizer and binder are:

$$T_{ox} = T_b \tag{6}$$

and

$$-k_{ox} \frac{\partial T_{ox}}{\partial x}\bigg|_{x_{if}} = -k_b \frac{\partial T_b}{\partial x}\bigg|_{x_{if}} \tag{7}$$

The heat conduction and transpiration in the gas phase are expressed as:

$$\rho_g c_g \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k_g \frac{\partial T}{\partial x}\right) + \rho_g c_g v_g \frac{\partial T}{\partial x} + \ddot{q}_g \tag{8}$$

Thus, the temperature profiles in the gas phase will depend on gas properties determined from simple kinetic theory. The gas phase chemical reaction ($\ddot{q}_g$) will be estimated from the granular diffusion theory. The flame zone thickness is defined as:

$$\frac{T_f - T_{fzt}}{T_f} = 0.95 \tag{9}$$

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Accordingly, at the distance x_{fzt} from the regressing surface, the temperature gradient is assumed to be zero or:

$$\left.\frac{\partial T}{\partial x}\right|_{x = x_{fzt}} = 0 \qquad\qquad (10)$$

(U)   There have been numerous efforts to solve the above equations for special cases. It is believed that the above relationships include the important parameters and incorporate empirical relationships for which constants are available.

(U)   The differential equations that consider the interactions between the gas phase and the solid phase reactions have been programmed for solution on a digital computer. Calculated burning rates obtained for ammonium perchlorate using the present form of the solution agree reasonably well with experimental data. The check-out of subsurface exothermic reactions and surface regression is complete.

(U)   In the process of performing calculations to determine the relative magnitudes of and the interactions between the subsurface reactions, the surface reactions, and the gas phase reactions, several defficiencies in the model have been uncovered. The analytical results have reaffirmed the importance of the endothermic reactions near the propellant surface as the rate controlling mechanism. However, the gas phase thicknesses that are being calculated are not as great as those measured by Sutherland (14). This discrepancy is believed to be caused by the manner in which the depletion of the reactable material in the gas phase is considered. Accordingly, the solution is being extended to more accurately account for the heat released in the gas phase immediately above the regressing surface.

(U)   When the above extensions have been made to the model, it will be in a form suitable for analyzing the several rate controlling hypotheses. Particular attention will be devoted to determining the effects of gas phase activation energies, chamber pressure, and ammonium perchlorate particle size on the propellant burning rate.

SECTION IV

CONCLUSIONS

(U)   In addition to the conclusions drawn in previous sections and those utilized in formulating a mechanism, the following conclusions have been drawn from the individual experiments performed:

(C)   1.   All iron compounds examined are readily oxidized to iron (III) oxide under a variety of conditions of temperature, pressure, and oxidizing content of the surroundings.

(C)   2.   Volatilization of either ferrocene or butyl ferrocene probably does not occur in the combustion of composite propellants. It is probable tnat under the influence of high heating rates, these materials will be immediately oxidized from their ambient states.

(C)   3.   Oxidation of either ferrocene or butyl ferrocene results in extremely finely divided iron (III) oxide. The particle size, although not accurately measured, appears to be less than 1000 $\overset{\circ}{A}$.

(C)   4.   At atmospheric pressure and slow heating rate, no discernible interaction exists between iron (III) oxide and ammonium perchlorate.

(C)   5.   At atmospheric pressure, ferrocene and butyl ferrocene are either volatilized or oxidized, mos probably to iron oxide, before decomposition of ammor um perchlorate initiates.

(C)   6.   As ferrocene sublimes from an ammonium perchlorate surface, a thin film of Fe_2O_3 remains on the surface of the oxidizer.

(C)   7.   Ammonium perchlorate mixed with iron (III) oxide decomposes at approximately the same rate as a heterogeneous mixture of ammonium perchlorate and Fe_2O_3 (Fe_2O_3 sprinkled on top of the oxidizer surface in a crucible). Therefore, it seems that contact by Fe_2O_3 is not important in the increase of oxidizer decomposition rate.

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(C) 8. Ammonium perchlorate decomposes thermally by three distinct steps of varying activation energy. The initial decomposition involves less than 10 percent of the material and seems to be associated with the crystalline transformation at 240°C. The presence of iron (III) oxide results in complete decomposition at the temperature corresponding to initial ammonium perchlorate decomposition.

(C) 9. Irc ʼʼʼ ʼxide in the presence of hot mixtures of air and a ⅃mo   ⅃. reduced to Fe_3O_4. Similar results are obtained wit'   ne and butyl ferrocene.

(C) 10. Perᴗ.   ᴗ acid (72 percent) in the cold reacts only slightly with the iron containing catalysts in question.

(C) 11. The rate of decomposition of anhydrous perchloric acid is increased 15 to 25 fold on the surface of iron oxide over the rate of decomposition of pure acid.

(C) 12. Anhydrous perchloric acid and either ferrocene or butyl ferrocene deflagrate upon contact.

(C) 13. The heat generated from the oxidation of ferrocene or its derivatives is sufficient to initiate deflagration of ammonium perchlorate.

(C) 14. Thermal decomposition of ammonium perchlorate under pressure occurs in a single-phase step instead of the three phases observed at atmospheric pressure.

(C) 15. As would be expected, both ferrocene and butyl ferrocene exhibit higher boiling points when heated under nitrogen pressure (200 psig).

(C) 16. The single-phase decomposition step of ammonium perchlorate is shifted to lower temperature in the presence of iron oxide. The degree of this shift is dependent upon Fe_2O_3 concentration.

(C) 17. Mixtures of ammonium perchlorate and either ferrocene or butyl ferrocene decompose under nitrogen pressure at a temperature preceding the crystalline phase transition of the oxidizer.

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(C)   18. More heat is evolved from the same weight of ammonium perchlorate when thermally decomposed in the presence of iron oxide than when decomposed alone.

(C)   19. Increased pressure results in increased exothermicity of ammonium perchlorate decomposition in the presence of iron oxide.

(C)   20. The decomposition temperature of ammonium perchlorate decreases with increasing iron (III) oxide content.

(C)   21. The autoignition temperature of composite propellant decreases with increasing pressure.

(C)   22. The presence of 0.5 percent Fe_2O_3 in a composite propellant substantially lowers the thermal decomposition temperature of the propellant. The effect is more noticeable than with mixtures of ammonium perchlorate and Fe_2O_3.

(C)   23. The rate of decomposition of anhydrous perchloric acid on varied surfaces seems to be a strong function of exposed specific surface of the catalyst and not overly dependent upon the chemical nature of the material.

(C)   24. Propellants containing iron oxide of varying specific surfaces exhibit burn rates which are functions of the specific surface of the catalyst; the higher the specific surface, the higher the burn rate.

(C)   25. The ease of oxidation of various ferrocene derivatives can be directly correlated with the initial temperature of ammonium perchlorate/catalyst mixture decomposition; the more readily oxidizable the catalyst, the lower the decomposition temperature.

(C)   26. The polymers cured with epoxides exhibit a preliminary slow rising exotherm at 150 to 200°C due to the post cure reaction of the carboxyl and epoxide and/or homopolymerization of the epoxide.

(C)   27. Both HA and HC gumstocks, independent of curing agents exhibit a broad exotherm peaked at 372°C. No weight loss is associated with this peak. It is believed that the exotherm at 372°C is due to further polymerization of the polymer through the double bond of the butadiene moiety.

(C)   28.   The heat release from homopolymerization of the binder (HC/MAPO) is increased in the presence of ferrocene or butyl ferrocene.

(C)   29.   Under nitrogen pressure, no preliminary decomposition of binder is affected by iron catalysts.

(C)   30.   Iron compounds such as Fe_2O_3. ferrocene and butyl ferrocene do not facilitate the pyrolysis of polybutadiene polymers or gumstocks.

(C)   31.   Increased pressure has no effect upon the temperature of initial decomposition of polybutadiene gumstocks.

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DOCUMENT CONTROL DATA - R&D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		

1. ORIGINATING ACTIVITY *(Corporate author)*	2a. REPORT SECURITY CLASSIFICATION
Thiokol Chemical Corporation	CONFIDENTIAL
Huntsville Division	2b. GROUP
Huntsville, Alabama	IV

3. REPORT TITLE

Investigation of the Mechanism of Solid Propellant Burn Rate   (U)

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Final Technical Report - 15 November 1965 through 14 November 1966

5. AUTHOR(S) *(Last name, first name, initial)*

Flanigan, David A.

6. REPORT DATE	7a. TOTAL NO OF PAGES	7b. NO OF REFS
	99	14

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
AF04(611)11212	
b. PROJECT NO.	AFRPL-TR-66-18
3148	
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	(Thiokol) 60-66 (Control No. C-66-60A)

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	Air Force Rocket Propulsion Laboratory
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	Edwards Air Force Base, Calif. 93523

13. ABSTRACT   The mechanism by which iron compounds catalyze the burning rate of solid composite propellants is reported. A series of experiments were conducted to define the efficacy of iron compounds on burning rate. Experiments performed under Phases I and II studies, which were designed to study the interaction, if any, between catalysts and oxidizer and binder indicate the following conclusions. Thermal decomposition of ammonium perchlorate under pressure occurs in a single-phase step instead of the three phases observed at atmospheric pressure. The single-phase decomposition step of ammonium perchlorate is shifted to lower temperature in the presence of iron oxide. The degree of this shift is dependent upon Fe_2O_3 concentration. The autoignition temperature of composite propellant decreases with increasing pressure. The rate of decomposition of anhydrous perchloric acid on varied surfaces seems to be a strong function of exposed specific surface of the catalyst and not overly dependent upon the chemical nature of the material. Iron compounds such as Fe_2O_3, ferrocene and butyl ferrocene do not facilitate the pyrolysis of polybutadiene polymers or gum-stocks. A mechanism for catalysis by iron compounds is presented and mathematical expressions relating the variables involved have been formulated.
  (Confidential)

DD FORM 1473
1 JAN 64

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Combustion						
Burn Rate						
Additive						
Chemical Mechanism						
Iron Compounds; i.e., Iron Oxide, Ferric Ferrocyanide, Ferrocene, Ferrocenyl Derivatives, Prussian Blue, n-butyl ferrocene (Thiokol Patent Secrecy Order Notice applies)						

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